JUL 22 1924

VOL. 10. JUNE, 1924 NO. 43

JOURNAL

OF

THE INSTITUTION

OF

PETROLEUM

TECHNOLOGISTS

AND

RECORD OF TRANSACTIONS.

FOUNDED 1913—INCORPORATED 1914.

PUBLISHED BY
THE INSTITUTION OF PETROLEUM TECHNOLOGISTS,
ALBERT HOUSE, BEDFORD STREET, STRAND, LONDON, W.C. 2,
AND PRINTED BY
W. SPRAGGET AND SONS, LTD.,
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All papers and articles submitted are assumed to be original communications unless otherwise stated, in which case reference to the previous publication should be given.

Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for publication in the Journal.

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Bibliography and Abstracts. A bibliography of current literature is published with each issue of the Journal, together with abstracts of the more important articles and patent specifications, this supplement being paged separately to the Transactions. In order to make this section of the maximum value, members are requested to send any matter which may have been inadvertently overlooked to the editor.

Medal for Student Members. A medal and a prize of five guineas will be awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented a paper of outstanding merit during the session.

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Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily. The additions made to the current and standard literature on petroleum and allied substances, since the publication of the last Journal, are :—

Handbook of Casinghead Gas. By Henry P. Westcott. 3rd edition. 1922.

Oil Engineering and Finance. Vols. I. and II., 1922.

Directory of American Institute of Mining and Metallurgical Engineers, Inc : corrected to April 7th, 1924. No. 209, May, 1924

From F. G. Rappoport :—

Government Geological Survey in Siam, 1923. Reconnaissance Geological Report of the Provinces of Pukat, Surashtradhani, Nakon Sridhamaraj and Patani, in Siamese Malaya. By Wallace Lee.

From E. DeGolyer :—

World Production of Petroleum in 1923.

From Dr. Victor Henny :—

Cracking Process aids Industry. The Dubbs Process for Cracking Oil. The Cracking of California Kerosene Distillate Oil. The Cracking of California Gas Oil. Results of Cracking Mid-Continent Fuel Oil, by the Dubbs Process. Results of Cracking Kentucky Fuel Oil, by the Dubbs Process. Refining Cracked Distillates vs. Light Oils. The Congealing Temperature and other Fuel Characteristics of Cracked Residue. Operating Practice in Refining Cracked Petroleum Distillates. The Acid and Fullers Earth Treatment of California Cracked Distillates. The Cracking of Wax Distillate Oil. The Cracking of Petroleum Oil in the Gas-Liquid Phase. Various Methods of Refining, with especial reference to Cracked Hydrocarbons Oils. The Cracking of Panuco Crude Oil. The Cracking of Venezuelan Fuel Oil.

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From Joint Board of the Universities of Manchester, Liverpool, Leeds, Sheffield and Birmingham :—

The Syllabus of Matriculation Examination, 1925.

For Review :—

From Ernest Benn, Ltd. :—

The Resources of the Empire Series. Fuel. By G. W. Andrew, M.Sc., F.I.C., 1924.

From McGraw-Hill Publishing Co., Ltd :—

Valuation of Oil and Gas Land. By R. W. Brown. 1st edition, 1924. A Textbook of Petroleum Production Engineering. By Lester C. Uren. 1st Edition, 1924.

From British Engineering Standards Association :—

Specifications to date. Copy of Report of the Unofficial Conference of the Secretaries of the Standardising Bodies in the various countries, held recently in Zurich, 1923.

From the Imperial Mineral Resources Bureau :—

Minerals of the Empire. British Empire Exhibition, Wembley, 1924. Mineral Industry of the British Empire and Foreign Countries. Statistics, 1919-1921, for Molybdenum, Vanadium and Potash Minerals.

CANADA.

From Mines Branch, Department of Mines, Ottawa, Canada :—

No. 10 : Memorandum Series, February, 1924. Recovery of Petroleum by Shafts and Galleries at Pechelbronn, Alsace, France, and at Wietze, Hanover, Germany.

AMERICA.

From U.S. Bureau of Mines :—

Reports of Investigations. Department of the Interior. Serial No. 2582. The Distribution of Sulphur in Crude Petroleum. By N. A. C. Smith and D. D. Stark.

Reports of Investigations. Department of the Interior. Serial No. 2595. Properties of Crude Oils from California. By A. J. Kraemar and H. M. Smith.

Bulletin No. 210. Department of the Interior. Oil Shale: An historical, technical and economic study. By Martin J. Gavin, 1924.

From U.S. Bureau of Standards ;—

Department of Commerce. Circular No. 159. U.S. Government Master Specification No. 84. For Asphalt for Mineral Surfaced Roofing.

Miscellaneous Publications. No. 55. Dept. of Commerce. Weights and Measures. (16th Annual Conference, May 21-24, 1923.)

Specification No. 83. Circular No. 155. U.S. Government Master Specification for Coal-Tar Pitch for Waterproofing and Damp-proofing.

U.S. Government Standard Specification. No. 2.c. Technical Paper 323 A. For Lubricants and Liquid Fuels and Methods for Testing. 1924.

From U.S. Geological Survey. Department of the Interior.

Water-Supply Paper 498. The Lower Gila Region, Arizona. 1923.

Water-Supply Paper 511. Surface Water Supply of the United States, 1919–1920. Part XI. Pacific Slope Basins in California. 1923.

Natural-Gas Gasoline in 1922. By G. B. Richardson.

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Water-Supply Paper 489. The Occurrence of Ground Water in the United States. By O. E. Meinzer.

Water-Supply Paper 492. Summary of Hydrometric Data in Washington, 1878-1919. By Glenn L. Parker and Lasley Lee.

Water-Supply Paper 497. The Salton Sea Region. California. By John S. Brown.

The Council would be grateful to members who are authors of books on petroleum or on allied substances if they would kindly present a copy of their works to the Library of the Institution, and for review in the Journal.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. G. P. Chaplin has returned from Burma.

Mr. Carl Phillips is now in England.

Mr. N. A. Sutherland has arrived in this country.

Dr. J. A. L. Henderson is now in England.

The Council desire to place on record their thanks to the Rt. Hon. Viscount Cowdray, of Cowdray, for his kindness in presenting the sum of £100 to be used for the encouragement of Student Members of the Institution.

The Institution is indebted to Messrs. Vickers, Ltd., of Barrow, for a large framed photograph of the tank-steamer, *British Minstrel*, which has been placed in the Members' Room.

The Secretary will be glad to receive information as to the whereabouts of the following members:—W. T. ARNETT, J. A. CHOWN, D. L. HOUGHTON, ALBERT JEFFREYS.

BACK NUMBERS OF JOURNAL.

Members possessing available copies of Journals No. 9, 17, 19, 25, 27, 28 or 30 are asked to notify the Secretary, who is prepared to purchase such numbers at the published price.

STANDARDIZATION COMMITTEE.

The Report of the Standardization Committee of the Institution has now been published under the title of "Standard Methods of Testing Petroleum and its Products," and copies can be obtained from the Institution Offices at the published price of 6s., or to members of the Institution for distribution, and marked "complimentary," at 4s.

H. T. BURLS.

We regret to announce the death of Mr. Herbert Thomas Burls, which took place suddenly on April 17th, 1924. Mr. Burls, who was sixty-eight years of age, was an Original Member of the Institution. He was an officer of the Order of the British Empire, and a Member of the Institution of Mining Engineers, the Institution of Mining and Metallurgy, the Society of Chemical Industry, the Geologists' Association, the American Institute of Mining Engineers, the French Institution of Civil Engineers, and a Fellow of the Geological Society and the Royal Geographical Society. Since 1895 he was engaged in the inspecting and reporting on mining and petroleum properties in various parts of the world, and latterly was working on the desulphurisation of shale-oil. He was well-known in the petroleum industry and will be greatly missed by his many friends and associates.

GENERAL MEETINGS.

The General Meetings of the Institution during the Session 1924-25 (October, 1924, to May, 1925), will be held at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C. 2, at 5.30 p.m. on the *first* Tuesday in each month instead of on the second Tuesday as in the past.

No. 43. Vol. 10.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Seventy-Eighth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, on Tuesday, April 8th, 1924, Mr. Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng. (President) occupying the Chair.

The following paper was read :—

The Crude Oils of Burmah and Assam.

By W. J. Wilson, F.I.C., A.C.G.I. (Member).

I.—BURMAH CRUDE OIL.

The occurrence of Petroleum in Burmah has been known to Europeans for at least 200 years, and long before the modern developments of the fields, which may be said to date from the formation of the Burmah Oil Company in 1886, the oil was a familiar commodity to the natives, whose supply was won by means of hand dug wells.

The most intensively developed and productive field of Burmah so far is that of Yenangyoung, followed by Singu and Yenangyat, all in the vicinity of the Irawadi River, and 275–325 miles from Rangoon. The crude oils from these fields are closely similar in quality to each other, although the crudes from the two latter are somewhat richer in light fractions, and the corresponding distillate fractions from each are practically identical. They are characterised by their exceptionally high content of solid paraffins, which are present in such proportion as to cause the oil to set at temperatures below about 70° F. Above the setting point the oil is a mobile liquid (viscosity about 40 seconds Redwood at 90° F.). It is not a pure paraffin base petroleum, as it contains an appreciable quantity of asphaltum. The colour of Burmah Crude Oil is brown by transmitted light and green by reflected light; it possesses a pleasant odour and is almost free from water. The oil contains

extremely little sulphur, and that not in a deleterious form. The small oxygen content (not shown in the analysis), is accounted for mainly in the fractions of high boiling point, in compounds of resinous and asphaltic character. A very small amount—about 0·025%—of naphthenic acids occurs in the kerosene and intermediate oil fractions; the lubricating oil fraction is practically free from acidic bodies.

As with most other petroleums, little can be said concerning the constitution of the hydrocarbons which comprise Burmah petroleum, except certain of those of low boiling point, to which reference will be made later. All the liquid distillates are of high densities as compared with those of fractions of similar boiling point range from most other petroleums. This is consistent with the presence of more than average proportions of aromatic and other hydrocarbons of low hydrogen content.

Analysis.—The following is the ultimate analysis of a representative sample of mixed crude oil :—

Carbon	86·45 per cent,
Hydrogen	13·25
Nitrogen	0·2
Sulphur	0·1
Oxygen	—
	100·00

The oil contains 0·0035 per cent. of ash, which consists of the following constituents, approximately in descending order of quantity: iron, aluminium, silicon, manganese, zinc, sulphate, phosphate, with a little calcium and magnesium, and traces of copper, cadmium, sodium and nickel.

The specific gravity of the oil averages about 0·835.

Distillation, in absence of cracking, gives :—

Gasoline (to 160° C.)	28 per cent.
Kerosene (160°–300° C.)	35
Intermediate oil	6
Paraffin, M.P. 136° F.	5
Do. M.P. 125° F.	3
Do. Soft (Sweats)	2
Lubricating oil base	13
Residuum	8
	100

In practice the large local market requirements of kerosene and the comparatively small local consumption of gasoline cause the former fraction to be increased, with reduction of gasoline and intermediate oil.

The detailed analysis of a typical sample of crude oil, distilled into fractions of approximately 5 per cent. each, is shown below.

End of Fraction.	Temperature of oil in still, ° C.	Stillhead vapour temperature, ° C.
1	135	105
2	158	124
3	170	138
4	186	151
5	188	151
6	186	148
7	194	142
8	246	193
9	266	219
10	286	238
11	305	256
12	312	268
13	321	276
14	328	282
15	340	284
16	349	289
17	361	293
18	375	297
19	388	286

Fraction		1	2	3	4	5	6	7	8	9	10
Per cent. of crude		4·99	5·01	5·00	5·00	5·03	5·01	4·99	4·99	4·99	5·02
Specific gravity at 60° F.		0·7315	0·750	0·762	0·771	0·7785	0·788	0·798	0·8125	0·826	0·836
Initial boiling point, ° C.		39	50	73	85	98	115	130	150	176	200
Distillate below—											
100° C.	%	59	39	16	4	1	—	—	—	—	—
125° C.	%	84	70	61	51	29	11	—	—	—	—
150° C.	%	92	87	81	75	64	49	19	—	—	—
200° C.	%	97	95	95	95	91	88	77	10	22	—
250° C.	%	—	—	—	—	97	97	95	90	80	57
300° C.	%	—	—	—	—	—	—	—	97	96	92
Final boiling point, ° C.		202	213	218	244	260	262	283	310	325	—
Flash point, ° F.		—	—	—	—	—	—	71	103	137	166
Setting point, ° F.		—	—	—	—	—	—	—	—	—	—

Fraction		11	12	13	14	15	16	17	18	19
Per cent. of crude		4·99	5·14	5·13	4·72	5·25	4·07	4·64	4·99	6·43
Specific gravity at 60° F		0·844	0·8515	0·857	0·8605	0·8665	0·8705	0·876	0·8815	0·8975
Initial boiling point, ° C.		223	241	260	275	300	—	—	—	—
Distillate below—										
100° C.	%	—	—	—	—	—	—	—	—	—
125° C.	%	—	—	—	—	—	—	—	—	—
150° C.	%	—	—	—	—	—	—	—	—	—
200° C.	%	—	—	—	—	—	—	—	—	—
250° C.	%	30	5	—	—	—	—	—	—	—
300° C.	%	84	72	55	25	—	—	—	—	—
Final boiling point, ° C.		—	—	—	—	—	—	—	—	—
Flash point, ° F.		195	212	232	260	288	304	326	334	362
Setting point, ° F.		—	44	54	41	71	87	101	113	122

In this instance five gallons of the oil were distilled without any fractionating column. Above 150° C. (vapour temperature) steam was used, and the last 40 per cent. was distilled under reduced pressure. Such a distillation enables a fair comparison to be made with distillations of other oils made by other operators. It has the disadvantage, however, that to estimate gasoline and kerosene redistillation is necessary. It is ordinarily preferred to prepare these products in a single operation by distillation over a column. The apparatus used by the author for evaluating crude oils is shown in Fig. 1. The quantity distilled is 20 or 25 litres, according to the nature of the oil. The usual procedure is to cut

the distillate at suitable points as indicated by the temperature at the top of the column, or that portion of the column which is in use. By mixing aliquot parts of the fractions obtained the quantities of gasoline of various grades which can be produced from the crude are readily ascertained and their specifications determined. The kerosene distillate may be similarly divided into two or more fractions, according to the grades required, or according to the different treatments which may be necessary for the fractions. For the fractions beyond kerosene the column is cut out, the vapours being led direct to the condenser.

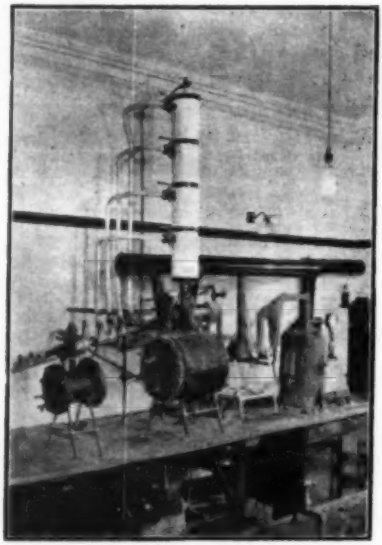


FIG. 1.

Refining.—The methods of refining followed in Burmah have already been described before the Institution by Mr. Andrew Campbell,* for many years the Works Manager of the Burmah Oil Company, Ltd., and are set forth in greater detail in the latter's "Petroleum Refining."

The system of fractional distillation and atmospheric condensation designed by H. L. Allan,† the present Works Manager of the Burmah Oil Company, Ltd., is being successfully developed.

* A. Campbell, Journ. Inst. Petr. Techn., II., No. 8, p. 274.
† Brit. Patents Nos. 177, 277, 149,776 and 152,791.

By this process (Fig. 2) products of required specifications are obtained in a single continuous operation, which as long as the same products are required is almost automatic. The only re-distillation required is that of the blue oil, following filtration of paraffin, into the various grades of lubricating oils.

The unit shown in the figure has a working capacity of about 120,000 gallons of crude per 24 hours. The plant has the advantage of exceptional flexibility.

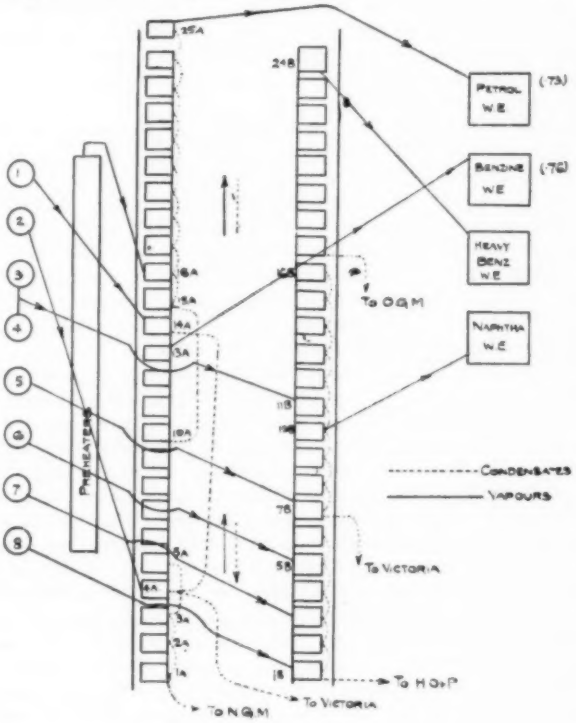


FIG. 2.

DIAGRAMMATIC ARRANGEMENT OF BENCH X.
N.B.—CASCADING. 15A TO 10A, 14 TO 4A, 5A TO 3A.

The crude oil passes through the pre-heaters, where it loses a portion of the volatile constituents, and thence to the stills 1 to 8 in turn, the oil in which is maintained at constant temperatures, higher at each stage, so that a distillate fraction is volatilised at

each still. Steam is used as with other apparatus. The vapours are led to the "boxes" (1A to 25A and 1B to 24B), which consist of comparatively small vessels arranged in gradually ascending levels from 1A to 1B upwards, and fitted with gauge glasses. The tops of the boxes are connected by vertical atmospheric condenser pipes for passage of vapours and by direct pipes for the passage or "cascading" of condensates. These pipes are open or closed by valves as may be required. Supplementary heat is supplied to the boxes as required by either closed or open steam, the lower temperatures being at the higher levels, as will be seen from the vapour lines shown in the figure. Hence oil volatilised from the boxes travels in an upward direction and vapours are led to condensers at suitable points.

Burmah petroleum does not readily undergo decomposition by cracking, so that with ordinary care the oil may easily be distilled down to coke without any appreciable breaking down of the heavier oils to oils of lower boiling-point or to gas. It is found, however, that in the absence of cracking the character of the distillates, particularly of the lubricating oil fractions, may vary considerably, the more complex molecules being apparently liable under certain conditions to undergo a rearrangement of their constitution, which renders them less stable chemically under normal conditions of their practical application.

Experience in the refining of this oil makes it appear probable that some crudes which have been regarded as being unsuitable for production of lubricating oils could, with a closer study of conditions of distillation, become satisfactory sources of such products.

It is well known that many crude oils which contain paraffin cannot be made to yield the latter in crystalline form, except under conditions involving cracking, and consequent sacrifice of a part of the paraffin and of the lubricating oil and probably also a lowering of the quality of the latter in some degree. This does not apply in the case of Burmah oils, at any rate those from the principal fields. Even if an excessive proportion of steam is used in the distillation, with or without reduction of pressure, the paraffin distils in good crystalline form, and is easily filtered. Only if the distillation is carried beyond the usual stage, when the paraffin is probably accompanied by other solid hydrocarbons of different constitution, does its character become partially amorphous.

The gasoline distillate is of pleasant odour, is practically free from sulphur and requires no treatment whatever. Of the kerosene, about two-thirds of the whole is readily rendered water-white by filtration through Bauxite, and indeed a portion, at least, of this also is a white distillate without any treatment whatever. The remaining one-third or so as a second quality kerosene, suitable for the requirements of the poorer classes of Indian consumers,

receives no treatment. Paraffin is obtained perfectly white by Bauxite filtration of the sweated scale, and lubricating oils are treated by the same agent, although a certain amount of acid is employed for these oils only. Incidentally the Burmah Oil Company, Ltd., own the Indian rights of the Oil Refining Improvement Company, Ltd.'s Bauxite patents, and that company has been responsible for their wide and successful application for the refining of mineral oils.

An apparatus recently introduced, which has given excellent results, is an improved form of sweating stove, the invention of

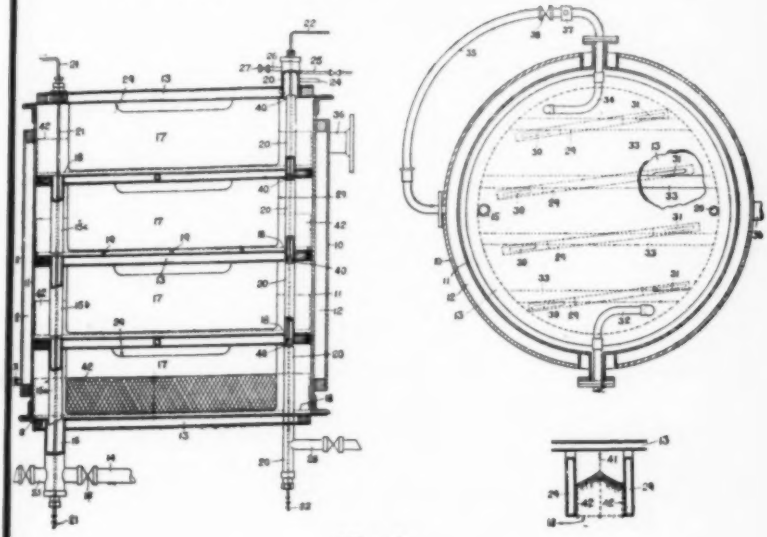


*Fig. 3.

*Reproduced from Patent Specification No. 208,195 by permission of the Controller, H.M. Stationery Office.

H. L. Allan and J. Moore,* the latter the Superintending Refinery Engineer of the Burmah Oil Company, Limited.

In this apparatus crystallisation and sweating of the paraffin scale are effected without the wax coming into direct contact with air. Highly accurate temperature control is secured, thus insuring the desired acicular type of crystalline formation and subsequent efficient sweating.

In Fig. 3 are shown a vertical section, horizontal section, and a

* Brit. Patent No. 208,195.

view showing the wax cake (partially sweated) between two heating elements.

The space 12 is a water jacket, and water or steam can be circulated through the cells 13, which are slightly inclined. The melted oil is supplied at 14, and fills the compartments 17 which rest on gauze 18. Air escapes or is admitted through the pipe 20, and pipe 23 is for running off sweatings and the finished product, and compartments 29 represent the heating elements. Hot water is first circulated through cells 13. The melted wax-oil mixture is led into the lowest chamber 17. When the latter is completely filled the other chambers 17 are similarly filled in succession.

The circulating water entering at 32 is then gradually cooled until crystallisation is effected.

Pipes 15a, etc., are cleaned by means of steam and sweating begun by raising the temperature of water circulating through cells 13.

Efficient drainage of the crystals is promoted by a gauze partition 41 set vertically along the centre of each space between the vertical elements 29, which are enclosed by gauze 42.

The apparatus enables any unevenness of working or occlusion of oil to be avoided, and a thicker cake than is customary can be dealt with. Its control is extremely easy. Owing to the high efficiency of the apparatus, the separation of oil is remarkably complete and the yield and colour of the wax considerably better than by other types of plant.

Products.

Gasoline.—The following is a typical distillation test of a gasoline cut at 160° C., representing 28 per cent. of the crude, and having a specific gravity of 0·757 :—

Initial boiling point	58° C.
Distillate below 100° C.	25¼%
,, ,, 125°	67%
,, ,, 150°	94%
Final boiling point	161° C.

As much as 16 per cent. of a high quality aviation spirit, end-point 130° C., can be obtained.

The content of aromatic hydrocarbons is not quite uniform, but the following analysis of the distillates may be taken as representative :—

	In distillate to 150° C.		In crude oil.	
	By weight.	By volume.	By weight.	By volume.
	%	%	%	%
Benzene	2·9 ..	2·5 ..	0·64 ..	0·60
Toluene	6·0 ..	5·2	1·31 ..	1·26
Xylene	6·8 ..	6·0 ..	1·50 ..	1·45
	15·7 ..	13·7 ..	3·45 ..	3·31

While no figure representing percentage of naphthenes is offered, it can be stated that these compounds represent a good proportion of the gasoline fraction.

The ultimate analysis of the gasoline distilling below 160° C. is

Carbon	85·8 per cent.
Hydrogen	14·2
	100·0

This represents an average composition of practically C_nH_{2n}.

The gasoline contains practically no olefines.

With the object of isolating individual hydrocarbons from Burmah gasoline, the portion boiling up to 110° C. has been subjected to a series of fractional distillations by F. Esling, who was able in this way to separate and subsequenty identify a number of compounds, all of which belong to the series of normal and secondary paraffins, penta- and hexa-methylenes and their derivatives, and the two aromatic hydrocarbons which are included in the range stated. As a full account of this work is in course of preparation by Mr. Esling, it is unnecessary to deal further with it in the present paper.

No liquid substances having boiling-points above that of toluene have to date been isolated from Burmah petroleum; it is well known that the number of possible isomers rapidly multiply as the complexity of the members of the hydrocarbon series increases, and separation of individual compounds becomes more and more laborious.

Kerosene.—Inasmuch as no method has yet been established for the determination of the several series of hydrocarbons having boiling points above 150° C., less is known of the composition of the kerosene fraction. Some indication of the nature of the oils which constitute Burmah kerosene is given by means of fractional solution in liquid sulphur dioxide. This solvent exerts a preferential solubility for aromatic hydrocarbons and probably others of low hydrogen content, but as far as the author is aware only partial separations have been attained by repeated fractionations made in this way. In a typical example, a kerosene of specific gravity 0·835 gave on treatment with liquid sulphur dioxide at 0° F.:—

75% of specific gravity	0·809
25% " "	0·914

The heavy hydrocarbons which are extracted by sulphur dioxide will not burn in a lamp unless with the formation of dense smoke, but their proportion in the first quality kerosene is not such as to render the latter unsatisfactory, as it burns normally and satisfactorily in an ordinary lamp. The unrefined yellow kerosene, consisting largely of the less volatile constituents, possesses lower illuminating value and more tendency to smokiness in burning.

The ultimate analysis of the kerosene fraction is :—

Carbon	86·5 per cent.
Hydrogen	13·5
	100·0

This represents an average composition $C_nH_{1\cdot87n}$.

Paraffin Wax.—The paraffin is usually marketed in grades having melting-points from 120°/125° to 140°/145° F. By means of fractional crystallisation from solution a number of members of the paraffin series have been separated, most of which correspond with hydrocarbons from other oils which have been identified by earlier investigators.

Melting pt. of fraction. ° C.	Probable identity.	Melting pt. of hydrocarbons. ° C.	Authority for hydrocarbon.
47·8 ..	$C_{23}H_{48}$ ..	48·0 ..	Mabery, Proc. Amer. Acad. **40**, 349.
53·6 ..	$C_{25}H_{52}$ ..	53—54 ..	Mabery, Proc. Amer. Acad. **37**, 565.
57·3 ..	$C_{26}H_{54}$ ..	56·8—57 ..	Krafft, Ber. **40**, 4783.
61·5 ..	?		
64·2 ..	$C_{29}H_{60}$ ..	63·6—64·1 ..	Do.
68·8 ..	$C_{31}H_{64}$ ..	68·4 ..	Do.
71·7 ..	$C_{33}H_{68}$ ..	71·8 ..	Do.
	or	or	
	$C_{34}H_{70}$ ..	71—72 ..	Mabery, Amer. Chem. J. **33**, 285.

Paraffins of higher melting-point than the above occur in bottom settlings and in sucker rod paraffin. From the latter a fraction melting so high as 91° C. has been obtained, but up to the present the composition of such fractions has not been investigated. Such high melting-point paraffins occur chiefly in the Singu field.

Lubricating Oils.—As shown by the analysis of the crude oil, the lubricating oils constitute a somewhat small proportion of the crude. The lubricating oil can, however, be fractionated into grades suitable for all classes of lubrication. Apart from their relatively high specific gravity, these oils possess no unusual characteristics.

The presence of substances of very high specific gravity in the lubricating oils is again shown by extraction with liquid sulphur dioxide, or more conveniently in the laboratory a solution of the latter in acetone. Two examples of such treatment of oils which were untreated distillates are shown :—

No. 1.—Spindle Oil.

	Original sample.	Extracted oil.	Residual oil.
Per cent.	— ..	16·4 ..	83·6
Specific gravity at 60° F.	0·9135 ..	1·0075 ..	0·985
Viscosity at 70° F.	229 ..	413 ..	204
,, 140° F.	56 ..	68 ..	54

No. 2.—Motor Oil.

Per cent.	— ..	11·1 ..	88·9
Specific gravity at 60° F.	0·946 ..	1·037 ..	0·937

Residuum.—Burmah residuum constitutes a good fuel oil, but has the disadvantage of being solid at ordinary temperatures. Consisting largely of paraffin, it cracks readily under pressure at a low cracking temperature, giving a good liquid fuel of low setting point and a colourless spirit which does not deposit gum on standing for about four years.

Other Burmah Crude Oils.—Two crude oils, at present produced only in relatively small quantities, are those of Yethaya and Palanyon. These oils are of interest in that, being closely similar to each other, they differ notably from the other Burmese oils. The two oils occur in close proximity. Practically free from asphaltum, they distil to a residuum of petrolatum, which, if further distilled, yields a distillate still largely amorphous. These oils contain in some cases little or no gasoline. Analysis of representative samples are as follows :—

	Palanyon.		Yethaya.
	Sample 1.	Sample 2. (normal).	(normal).
Specific gravity	0·875	0·911	0·930
Water	—	0·2%	0·2%
Distillate below 150° C.	15½%	3%	nil
Distillate 150° to 300°	59%	46%	32%
Intermediate and lubricating oils ..	20½%	26%	33%
Petrolatum	nil	25%	35%

The small field of Yenanma produces oil closely resembling that of Yenangyoung.

Burmah Natural Gas.—Natural gas in Burmah is conserved as much as possible, and its further conservation is a subject for constant study and care. The production is being utilised to a notable extent as fuel for the power house where electrical energy is generated for drilling, pumping, etc. Further development of its utilisation as fuel and for gasoline extraction is now rapidly proceeding.

Of a few gas analyses which are available, the following is a summary of the results :—

	per cent.		per cent
Methane	Highest .. 87·7 / Lowest .. 47·9	Average ..	69·3
Ethane	Highest .. 49·1 / Lowest .. 9·8	Average ..	23·7
Carbon dioxide	Highest .. 2·9 / Lowest .. nil	Average ..	0·8
Oxygen	Highest .. 7·4 / Lowest .. nil	Average ..	2·7
Nitrogen (by difference).	Highest .. 13·5 / Lowest .. nil	Average ..	3·5
			100·0

The above analyses include both wet and dry gases, paraffin hydrocarbons being calculated to terms of methane and ethane.

Another set of analyses of dry gases only gives the following average :—

Methane	77·7 per cent.
Ethane	10·2
Carbon dioxide	nil
Oxygen	nil
Nitrogen	12·1
	100·0

Gasoline is extracted from wet gas by compression prior to the utilisation of the gas as fuel, the average gasoline yield being about 1·8 gallons per 1000 cubic feet of gas.

II.—Assam Crude Oils.

The two chief producing oilfieds of Assam are those of Digboi and Badarpur. These fields are some 400 miles apart, and the oils are of totally different character.

Digboi Crude Oil.—The petroleum of Digboi (Assam Oil Co.) is very close associated with deposits of lignite, and is singularly free from water. It is of similar nature to Burmah petroleum, containing an even larger percentage of solid paraffins, but also more asphaltum than the Burmah oil. It is consequently darker in colour and of stiffer consistency at ordinary low temperatures. Its distillates are similar in quality to those of the latter, and are refined with equal facility.

The following is the ultimate analysis of the crude oil :—

Carbon	86·3 per cent.
Hydrogen	12·9
Sulphur	0·15
Nitrogen	0·2
Oxygen	0·45
	100·00

Below are the results of a laboratory analysis of a representative sample :—

Specific gravity at 60° F.	0·856
Completely fluid at 93° F.	
Viscosity at 93° F. : 42 seconds (Redwood)—	
Gasoline (to 160° C.)	16·8 per cent.
Kerosene (160–300° C.)	30·2
Intermediate oil	3·4
Lubricating oil base	10·8
Paraffin, M.P. 136° F.	7·6
Paraffin, M.P. 126° F.	3·1
Sweats, M.P. 96° F.	8·8
Residue	19·3
	100·0

Analysis of distillate below 150° C. :—

			Calculated to crude oil.
	%		%
Benzene	4·6 by volume	..	0·7
Toluene	7·3 „	..	1·1
Xylene	7·6 „	..	1·15
	19·5		2·95

The ash of Digboi petroleum amounts to about 0·01 per cent., and consists (in approximately descending order of quantity) of oxides of iron, aluminium, magnesium, calcium, barium, and sodium, with small amounts of sulphate, phosphate and silicate.

Badarpur Crude Oil.—The Badarpur field, which was opened up by the Burmah Oil Co., is of particular interest, the petroleum being somewhat in the nature of a " freak " oil. The field contains many water sands, and the oil has in its history probably been in constant association with water. A sand of comparatively light oil occurs between higher and lower sands of heavy oil.

Badarpur crude oil is characterised by the following properties :—

(1) It is a natural fuel oil, excellent as regards viscosity and other properties as it comes from the well.
(2) Exceptionally high specific gravity.
(3) In the case of the majority of wells producing from the earlier sands, absence of gasoline.
(4) Total absence of solid paraffins, and only very little asphaltum.
(5) The solid residuum from distillation is brown, resembling rosin rather than asphaltum.
(6) Poor lubricating quality of the heavier distillates, which is not corrected by chemical treatment. The later fractions from some samples are as adhesive as glue, and have a specific gravity above unity.
(7) Unusual chemical constitution of certain hydrocarbons which have been isolated.
(8) Very pleasant odour resembling somewhat that of camphor.

The ultimate analysis shows an exceptionally low percentage of hydrogen ; this is consistent with the high specific gravity :—

Carbon	88·8 per cent.
Hydrogen	10·8
Sulphur	0·1
Nitrogen	0·2
Oxygen	0·1
	100·0

This represents a hydrocarbon composition of $C_nH_{1\cdot47n}$, which is entirely unlike ordinary proportions. The content of asphaltum as determined by the ordinary methods is about 0·1 per cent.

The limitations of accuracy of an ordinary analysis in which oxygen is determined by difference leave a value of almost *nil* for oxygen, but oxygen is probably present in the oil, though evidently not to the extent to which the gummy character of the oil would lead one to expect. It would seem that the resin-like substances which represent a large proportion of the heavier fractions are unsaturated hydrocarbons of high molecular weight, associated with a small proportion of oxygen compounds.

The results of a distillation into 5 per cent. fractions are shown below :—

Fraction	1	2	3	4	5	6	7	8	9	10
Per cent. of crude (by volume) ..	5·03	4·96	4·93	4·86	5·08	5·27	4·96	5·01	4·87	5·01
Specific gravity at 60° F.	0·881	0·8945	0·907	0·913	0·920	0·928	0·935	0·944	0·956	0·9675
Initial boiling point, ° C.	178	201	213½	224	233½	244	257	268	278	—
Distilling below 200° C. %	20	—	—	—	—	—	—	—	—	—
Distilling below 250° C. %	78	70½	58	45	29	5	—	—	—	—
Distilling below 300° C. %	93½	91½	90½	88	81½	78	70	61	39	—
Flash point, ° F. ..	126	154	172	186	198	212	222	234	248	266
Viscosity (Redwood-secs.)										
At 70° F.	—	—	—	—	—	—	—	—	—	116
At 100° F. ..	—	—	—	—	—	—	—	—	—	62
At 140° F. ..	—	—	—	—	—	—	—	—	—	41
At 200° F.	—	—	—	—	—	—	—	—	—	—

Fraction	11	12	13	14	15	16	17	18	19
Per cent. of crude (by volume) ..	4·96	5·12	5·05	5·24	4·65	4·71	4·61	4·44	5·17
Specific gravity at 60° F.	0·981	0·9945	1·0035	1·0145	1·0245	1·036	1·039	1·051	1·052
Initial boiling point, ° C.	—	—	—	—	—	—	—	—	—
Distilling below 200° C. %	—	—	—	—	—	—	—	—	—
Distilling below 250° C. %	—	—	—	—	—	—	—	—	—
Distilling below 300° C. %	—	—	—	—	—	—	—	—	—
Flash point, ° F. ..	282	304	320	336	354	360	358	320	346
Viscosity (Redwood-secs.)									
At 70° F.	194	373	820	1942	6830	—	—	—	—
At 100° F.	83	126	225	404	892	2508	—	—	—
At 140° F.	47	56	75	105	169	311	724	3228	—
At 200° F.	—	—	—	—	—	61	91	188	392

The sample here examined is typical of most of the oils from those horizons of this field which contain no gasoline. Its specific gravity at 60° F. is 0·9775. The usual range of specific gravity of the oils from different wells is from about 0·930 to 0·990, but there are a smaller number of wells producing lighter crudes containing a small proportion (up to about 12 per cent.) of gasoline. The topped oils from these crudes resemble the normal crude oils. The distilling points of a sample of the gasoline (specific gravity 0·7585 at 60° F.) are shown :—

Initial boiling point	74° C.
Distillate below 100° C.	26%
„ „ 125°	83%
„ „ 150°	98%

The high density is not due to predominance of aromatic hydrocarbons, as these compounds are present in relatively small proportions :—

Benzene	..	0·9% by volume of gasoline.
Toluene	..	1·4%
Xylene	..	2·5%

Total aromatics to 150° C., 4·8%, representing about 0·5% of the crude oil.

A fraction of suitable boiling-point range constitutes a white spirit which has the virtue of drying more rapidly than other distillates of similar boiling points.

The author is indebted to Dr. F. B. Thole for an account of an investigation of much interest of the fraction distilling between 160° and 270° C. The fraction was refractionated twice and concentrations of distillate were observed at 170°–180°, 190°–200° 220°–230° and 250°–260°. The percentages of carbon and hydrogen and the molecular weights of these fractions were determined, from which results the composition of the fractions was deduced.

Fraction.		Specific gravity at 60° F.		Composition.
170°–180°	..	0·848	..	$C_{12}H_{22}$
190°–200°	..	0·868	..	$C_{13}H_{24}$
220°–230°	..	0·888	..	$C_{14}H_{26}$
250°–260°	..	0·900	..	$C_{15}H_{28}$ and (less) $C_{15}H_{28}$

The first three fractions, which had a pronounced camphoric odour, are homologues of the series C_nH_{2n-2}, also the lesser part of the last fraction, the other compound being of another type. The fourth fraction had also a different odour.

These hydrocarbons are attacked only slowly by fuming sulphuric acid.

The ash of Badarpur crude oil amounts to *nil* to 0·2 per cent. of the crude oil, and contains (in approximate order of quantity) oxides of iron, aluminium, zinc, magnesium, and calcium, with small proportions of sulphate, phosphate and silicate.

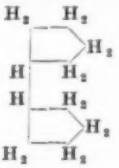
In conclusion, the author wishes to express his thanks to Mr. T. Dewhurst, Chief Geologist of the Burmah and Assam Oil Cos., Major J. A. Carpenter, Chief Research Chemist, the Burmah Oil Co., Syriam, and the gentlemen already mentioned, who have supplied data of much interest, to the members of the staffs of the Research Laboratories of the Burmah Oil Co., Ltd., at Syriam and at Forest Hill for many of the results recorded, and to Mr. R. I. Watson, Managing Director of the Burmah Oil Co., Ltd., for valuable suggestions and for permission to publish this paper.

DISCUSSION.

Dr. A. E. Dunstan, in opening the discussion, said there were two particular reasons why he welcomed the opportunity of saying a few words in connection with the paper, the first being that his colleagues and himself had been associated with the author on many occasions in carrying out investigations in respect to the chemistry of Burmah crude oils, and secondly, and more particularly, because he desired to take the present opportunity of acknowledging the thanks of the members to the author for the work he had done in connection with the valuable bibliography of the Journal. When he (Dr. Dunstan) took over the editorship of the Journal, commencing with Number 21, one of the first things he decided to do was to publish a bibliography, the first few issues of which were contributed by Mr. Campbell. When Mr. Campbell had to give up the work, Mr. Wilson took his place, and speaking editorially, he could only say that Mr. Wilson's copy always arrived with extraordinary punctuality and regularity. He was sure the members would greatly appreciate what the author had done in that direction.

With reference to the paper, he thought the author had made a very valuable contribution to the quantitative data which existed at the present moment in regard to the various crude oils of the world. During the nine and a-half years of the history of the Institution, it was a curious thing that the only papers which had been contributed in relation to crude oil referred to the East Indies, Egypt, Persia and Burmah and Assam. He hoped it would be possible in the near future to obtain a very much more comprehensive list of papers dealing with that most important subject. As he had stated at previous meetings of the Institution, the time was coming—and was possibly not far distant—when some of the crude oils of the present day would be curiosities, so that the sooner the Institution obtained particulars of their chief physical and chemical data the better it would be. He desired to refer to very few points in the paper itself, particularly as the Institution was honoured by the presence of Mr. Allan, the manager of the Burmah Oil Company at Syriam, who he hoped would give further details of the extraordinary efficiency of the fractionating plant associated with his name. He desired, however, to draw attention to one or two matters connected with the ash analysis from various oils which the author had described. For some time past there had been a gradually increasing interest in the nature of the ash of

petroleum, largely brought about by a paper read by Mr. Hackford,* and he knew quite a number of chemists who were busy at the present moment in this investigation. The author had pointed out that two of the oils contained nickel, which in itself was a very interesting point. In that connection he desired to draw the attention of the members to a paper by William Ramsay which appeared in the current number of the Journal.† Whether Ramsay used perfectly recognisable samples of Burmah oil he did not know, but he noted that nickel existed to the extent of 12 parts per million in what he called thin Burmah crude, and 8 parts per million in heavy Burmah crude, and as the ash was 35 parts in a million, that was a very considerable ratio of the total ash content. Perhaps the author could clear up that discrepancy, because nickel apparently, from his analysis, was a minor constituent of the Burmah oil. Another point upon which he would like further information was the statement that cadmium was identified. If that was the case he thought it was quite a unique phenomenon, because he did not remember having previously heard of the presence of cadmium in the ash of a mineral oil. If it did occur it would be extraordinarily interesting to search still further in the sedimentary rocks associated with the oil horizons. It was just conceivable that the presence of cadmium might be due to an error in the analysis, arsenic, for example, being taken for it. It would be most useful if the author would give the quantitative figures of the ash analysis for the purpose of record. The last point to which he wished to refer related to the Badarpur oils. Those oils were of a curiously non-reactive nature. He believed Dr. Thole came to the conclusion that the possible formulation of the first member of the series was of the following nature :—



The chemical behaviour rather suggested such formation; for example, it resisted nitric acid in sealed tubes, but he did not feel quite so sure about it after seeing the author's viscosity figures. The members would have noticed in the fractions of the Badarpur oil which the author examined that there was a remarkably steep viscosity curve.

* "The Significance of the Interpretation of the Chemical Analyses of Seepages," Journ. Inst. Petr. Techn., 8, p. 193, 19 .

† "The Significance of Nickel in Petroleum," Journ. Inst. Petr. Techn., 10, 41, p. 87, 1924.

The viscosity went down with the temperature very much more sharply than would be anticipated for a simple hydrocarbon of that nature, so much so that one would be inclined to predict from the viscosity figures that those particular hydrocarbons were closely associated, and it was not likely that a compound of that formulation would associate materially. He hoped the author would give his views in regard to the constitution of those substances.

Mr. H. L. Allan said he did not anticipate when he attended the meeting that he would be asked to speak, and as a result he had no data with him. The paper referred to plants that were in operation, but unfortunately the author was not aware of further information and material which were available and might have been placed before the members. For instance, the chart he had shown could have been supplemented by photographs which would have given a clearer conception of the distillation plant. The only addition he wished to make to the author's remarks with regard to the atmospheric system was that he did not think Mr. Wilson had brought out clearly that the preheating was done by the vapours more than by the residue, for the reason that the quality of the Burmah crude was such that practically everything was merchantable as a superior product, and was therefore a distillate.

In the atmospheric bench equipped with preheaters they were now distilling through one unit about 1200 tons a day, taking off 93 per cent. distillate, all of it finished product—*i.e.*, they took off petrol which has a composition of about 0·730 specific gravity, initial boiling point 37° C., final boiling point 142° C., containing over 80/90 per cent. under 100° C. This quality is aviation spirit. The next fraction which came off the same side of the atmospherics had a gravity of approximately 0·755 to 0·760. The specification for this spirit is 20 per cent. under 100°, with final boiling point 184°, but the apparatus usually delivered a spirit much superior in quality, having, say, 35 per cent. under 100° and a final boiling point of about 160° C. A larger quantity could be made, reducing these percentages, but this would entail a rise in gravity beyond the specification.

It was on this product that the chief claims had been made for atmospherics. In straight distillations performed by various chemists, the Author, Dr. A. E. Dunstan, Dr. S. J. M. Auld and others, they had been unable to produce the results obtained by atmospherics without blending the fractions—*i.e.*, they took off a series of 2 per cent. fractions, say, 10 or 12; they removed the fraction which contained the aromatics and blended it with the heavy spirit fraction, otherwise they could not get a spirit with the necessary content of 100° C. In a straight distillation under

dephlegmators, taking off spirit to 0·725 gravity, the content under 100 would be about 90 per cent., the final boiling point much the same as the atmospheric spirit, but when they continued on to the heavy spirit it contained practically nothing under 100. Thus, automatic blending is one of the claims made for the apparatus.

One of the theories he had advanced which had not been disproved was that the aromatic hydrocarbons did not go forward with paraffins of a corresponding boiling point. Analysis had proved that the light spirit produced under a dephlegmator contained very much more aromatic hydrocarbon than a spirit of similar gravity produced by atmospherics. Using the latter apparatus, the bulk of the aromatic benzol toluene was relegated to the heavier spirit where one would not expect to find it, as the 0·725 spirit, going off beforehand, should contain at least the benzene fraction, but in practice this did not happen. Analyses had been made by Major Carpenter and others and were, he thought, correct. He put forward the theory first of all that the specific heats had something to do with the phenomenon, but he was afraid that was not a tenable position. Although in the works plant they were actually producing 20 per cent. of motor spirit, which was as much as any distillation plant or method had ever taken out of the crude, yet, when the kerosene fractions which followed were analysed they were found to contain quite substantial proportions of spirit boiling under 150° C. Such fractions could not be included in the heavy spirit because of their high gravity. It was evident that there was a good deal in the system of fractional condensation that was not quite understood and would repay further study. The time in which the vapours were allowed to travel through the apparatus was an important factor.

Passing to kerosene, lubricating oil, heavy oil and paraffins, the claims made for the apparatus were that these products in being distilled were condensed fractionally in each unit, but with the ordinary apparatus, using an intermittent still or a still in which the whole of the vapours were condensed in bulk, the products were not so good, as they were liable to contain any cracked distillate. Heavy vapours entered the atmospheric system which might be compared to a row of bottles, the tube leading out from each bottle to the next one and arranged so that the condensates in each bottle could cascade back from unit to unit so that the products desired were obtained from these bottles and the cracked product, which was usually more volatile, passed on to the condenser and was so eliminated. By such means they had been able to produce from Burmah crude, lubricating oils that had not been surpassed, using a vacuum equivalent to 40 mm. absolute pressure. The residue left in the crude oil stills was about 7 per cent., and it probably contained 15/20 per cent. asphalt. It did not pay to

continue the distillation any further, as the paraffin in the distillates beyond this point tended to be amorphous and therefore difficult to separate.

The whole distillation was a continuous operation in a series of stills of 40 tons capacity each, and the method of firing was by means of central flues—*i.e.*, the Lancashire boiler type. They had been able to construct these stills so that they had already run over six months at the throughput cited, down to a residual gravity of 0·960 without any trouble from coke or other difficulty.

With reference to the other apparatus mentioned, the stove, so far the plant in being, was an experimental unit of about 1000 gallons capacity, but the results from this unit had been so satisfactory that the Burmah Oil Company were proceeding with the erection of 24 units of large capacity. The design of this apparatus was dictated by the fact that all the other paraffin plants on the market gave results that were more or less unsatisfactory. In designing this plant the objects aimed at were to obtain an apparatus in which the cooling and sweating would be capable of very close control, and as the whole operation of cooling and sweating is conducted by water this has been obtained. In addition, it occurred to the speaker that the old system of supporting the wax cake in a tray with a gauze raised slightly from the floor and filled up with water to that level was not necessary. In this apparatus there is no water below the gauze, and it is found in operation whenever sweating is started the space between the tray and the gauze clears very rapidly. Further, the apparatus, being completely closed, does not suffer from the usual disadvantages of dirt and dust, and there is no leakage—in fact, the apparatus is practically foolproof. In operation the plant is filled from the bottom, the liquid wax rising up from cell to cell. During the time of charging, hot water above the temperature of the liquid charge is circulated, and this continues until the apparatus is full. The circulating water is then gradually reduced in temperature until an envelope of wax is created in each cell, when the temperature of the circulating medium can be reduced more rapidly. The charge is not cooled down until the whole mass is perfectly solid, as it is found that better sweating is obtained if cooling is not carried too far, the temperature, of course, being contingent on the quality and melting point of the charge. To illustrate the value of the apparatus for the purpose for which it is designed he would quote a few figures.

A mass of wax was charged into the stove, melting point of the charge being 137° F.; 50 per cent. was sweated from it, giving a residual product of 144° F. melting point. The 144° wax was recharged and 50 per cent. of it sweated, the rise in temperature from the beginning of the sweating to the end being 1½°. A product

50 per cent. had a melting point of 145½°. Candles made from this wax gave a bending point of 139° F., whereas candles made from a wax of 140½° melting point obtained by the old system had a bending point of 121½° F. This seems to prove conclusively, he thought, that the wax was very homogeneous. As already mentioned, the control of the plant is by circulating hot or cold water. Steam is only used to rapidly melt out the product.

Mr. E. H. Cunningham-Craig desired in the first place to congratulate the author upon the very interesting paper he had given, the interest of which had been greatly enhanced by the account Mr. Allan had just given of his apparatus in use at Syriam. It was quite evident to him that Syriam had advanced a very great deal since he first went round the works there. There were a few points in the paper on which he would like to obtain further information from the author, particularly in regard to the different crude oils that existed in Burmah. Could the author give any account of the differences in the oil in the Yenangyoung field as one went deeper and deeper into the series? He knew there were slight differences in the oil, but he had never seen any real account of the differences that existed as one went from sand to sand downwards. The great trouble was that all the oils were poured into the same tanks, sent down the same pipe-line, and mixed up with oils from other fields; but he was sure some records must exist of the changes that occurred in the oils as the lower sands were reached. Such points were very interesting to geologists, who were always endeavouring to ascertain the history of oils from their various qualities and characters. In the same way there were two crude oils at Yethaya. The first one was supposed to be a very heavy oil having a specific gravity of 0·98, which occurred on a terrace structure round the dome, but there was a lighter oil which occurred at a lower horizon, being obtained mostly towards the centre of the dome at Yethaya, and he believed it was the second oil of which the author had given an account in his paper. There was another very interesting oil which occurred only in a few shallow wells on the eastern side of Twingon, but he supposed that had been exhausted a long time ago. That was also a very heavy oil, and different from the normal crude oil of Yenangyat. He believed it made a very good lubricating oil; in fact, he believed it could be used in its crude state for lubrication.

A Member, interposing, said that that oil was obtained from dug wells mostly.

Mr. Cunningham-Craig said that he knew the old Twingon oil perfectly well, as he remembered cleaning his rifle at school with it;

but he thought the oil in the shallow wells on the eastern side was rather different.

Dr. F. B. Thole said that the author had described in Badarpur petroleum one of the most extraordinary of crude oils. The whole of the fractions were markedly dissimilar from those obtained from other petroleums.

The speaker had had the opportunity of examining in some detail the fractions of lower boiling point, and found that they consisted not of paraffins or naphthenes of the usual type but of hydrocarbons with a most characteristic camphoraceous odour and of remarkable chemical stability. By careful fractionation he had isolated those with formulæ $C_{12}H_{22}$ (b.p. 175° C.) $C_{13}H_{24}$ (b.p. 195° C.) and $C_{14}H_{26}$ (b.p. 225° C.). These were undoubtedly homologues, but there was no direct evidence as to their constitution; possibly they were dicycloparaffins. After $C_{14}H_{26}$ there were indications that this homologous series ceased to exist in the oil, as the odour and analytical data altered sharply at this stage.

The unique viscosity-temperature decrement shown by the higher fractions and commented upon by Dr. Dunstan was clearly a characteristic of another type of remarkable hydrocarbons, for the series C_nH_{2n-2} referred to above seemed to become extinct at the fraction boiling at 260° C.

The entire absence of lubricating qualities in these very viscous higher fractions was most striking. Almost invariably it is found that high-boiling viscous petroleum distillates have an oily feel and are reasonably good lubricants. From this petroleum the corresponding fractions with high viscosity were sticky and in no way oily; in fact, to the touch they resembled resin or molasses rather than lubricating oil. In fact, this petroleum was the raw material for a wide series of researches of absorbing interest, as the whole of the products obtained from it were quite unique.

Mr. E. Lawson Lomax said he had recently come across another oil, of a very similar nature to Badarpur oil, which was found in Central Europe in a small field producing about 150 tons a month. He saw the experiments carried out on the Badarpur oil some time ago, and he had also seen the analysis made of the other oil from Egbell, in Czecho-Slovakia, and to all appearances both oils were similar. A method of refining the Czecho-Slovakian oil had been devised and used quite successfully, and high-class lubricants were being produced from it. The heavy fractions were quite sticky before refining, but the sticky compounds could be separated and very high-grade lubricants made from the oil. He had several samples of those lubricating oils in his laboratory which he would be pleased to show to any of the members who were

sufficiently interested in them. The author stated that the Assam oil was singularly free from water. His own experience was entirely different, the oil producing a quantity of water which it was quite difficult to get rid of at the beginning, as it was almost in the form of an emulsion, and required a long time to settle.

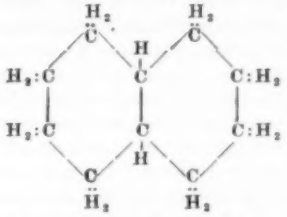
Mr. T. Dewhurst said that Mr. Cunningham-Craig had raised the very interesting point that the crude oils of Burmah and Assam dealt with in the paper were most of them mixtures of the crude oils from several, and in some instances many, oil-sands. As an example of that it was well known that in the Yenangyoung oilfield there were many oil-sands, and it was possible that there were slight differences in the character of the oil in those various sands. The members had had presented to them in the paper the characters of a mixture of the oils from all those sands. What applied to Yenangyoung crude applied to most of the other crude oils that had been dealt with. The author had pointed out that the crude oils of the Singu and Yenangyat fields were richer in lighter fractions than the Yenangyoung crude oil. It might be of interest in that connection if he pointed out that the Yenangyat crude oil was geologically older than Singu crude oil, and that both those crude oils were older at least than the oils from the upper oil-sands of the Yenangyoung field. So that it was possible that the differences in the crude oils of those different fields were due to the fact that the oils were of slightly different geological ages. The fact that the Palanyon and Yethaya crude was notably different from all other Burmah crude oils was most extraordinary, particularly when the remark made in the paper was borne in mind, that the crude oil of the small Yenanma field resembled Yenangyoung crude, because the Palanyon and Yethaya fields were situated midway between the Yenangyoung and the Yenanma oilfields. How was it that those fields situated between Yenangyoung and Yenanma should have oil which was notably different from the oils to the north and to the south ? That striking difference was not due to the existence of a peculiar oil at one definite geological horizon. It was certainly not due to that, because there were several thousand feet of beds between the Yethaya oil-sands and the Palanyon oil-sands ; so that that peculiar oil, which was different from all other oil in Burmah, occurred throughout a wide range of strata. He thought it almost followed from the evidence that the peculiar nature of the Palanyon and Yethaya crude was due to something quite local, something peculiar to those districts. It so happened that those two small fields occurred on an anticline which had been subjected to very intense earth movement, and it was probable that the oil-sands had been subjected to extraordinary compression, and as the oils were heavy it seemed to be possible that the intense earth

movement had so affected the crudes that perhaps some of the lighter fractions had escaped. He mentioned that as an interesting possibility.

Another very striking point about the paper was that there should be in Assam two oils so strikingly different as the crude oils of Badarpur and Digboi, and in rocks of roughly the same geological age. It was not the Digboi oil which was peculiar, because that oil resembled the Burmah oil and seemed to be quite normal. It was the Badarpur oil which was a very unusual oil—so unusual as to be described as a "freak" oil by the author. On the face of it it appeared that the difference between the crude oils in the Badarpur and the Digboi fields was probably due to differences in the original mother substance or substances from which the petroleums were formed. But there was one striking difference between those two oilfields. The Digboi field was devoid of water; on the other hand, the Badarpur field was quite different, containing numerous water-sands. He had seen references in papers to the effects of the inter-action of water and oil, and it seemed to be possible that although the main difference in the two oils was due to the original differences in the mother substance or substances from which the petroleums were formed, some differences might have resulted from the fact that one oilfield was free from water while in the other case the oil had been associated with much water. He desired in conclusion to express his gratification at the closer collaboration which existed nowadays between chemists and geologists than was formerly the case. Speaking from the geological point of view, he thought it would be not only most interesting but most valuable if geologists could be provided by chemists with a knowledge of the nature of the different crude petroleums which occurred at different horizons in an oil-series. Furthermore, he thought that in the future some work would have to be done on the variation of oil that occurred in one and the same geological horizon. Some work had already been done in that connection with very interesting results, principally in indicating the direction in which most of the oil migrated into the oil-field structure. He was sure all geologists welcomed any information they could obtain regarding the chemistry of crude petroleums, and therefore their best thanks were due to the author for the very interesting data respecting the crude oils of Burmah and Assam.

Mr. F. Esling said that some five years ago he had carried out some experimental work on Badarpur crude oil with Mr. W. Robertson. After some considerable time they came to the conclusion that the constitution was somewhat different from what Dr. Dunstan had demonstrated. He and his colleague had the advantage of Dr. Dunstan's and Dr. Thole's previous researches to

go upon, but owing to the fact that they had not been able to carry their work to the point they had desired, they had not as yet made known the results they had actually arrived at. They came to the conclusion that the oil had as its basis a constitution very similar to that of naphthalene, being hydrogenated to the full extent. That would correspond to a composition represented by



Decahydronaphthalene.

The refractive index, specific gravity and other properties of their earlier fractions resembled very closely that compound and its methyl and di-methyl derivatives.

The methyl groups could occupy any of the eight positions in which the carbon atoms are united to *two* H-atoms, or could substitute the H-atoms attached to the centralised C-atoms. Thus it is possible to get three distinct isomers of methyldecahydronaphthalene, and 17 isomers of dimethyldecahydronaphthalene, which latter would also be isomeric with the three ethyl-derivatives. One of their fractions had the same composition as that referred to by Dr. Thole, viz., $C_{12}H_{22}$; but exactly which of the 17 isomeric di-methyl compounds or of the three ethyl derivatives, or what mixture of any of these the fraction was composed of, they had not attempted to determine.

The first samples of Badarpur crude oil examined by Mr. Robertson and himself corresponded to that mentioned by Mr. Wilson with a specific gravity at 60° F. of 0·9775, and gave a first 5 per cent. fraction with a sp. gr. at 60° F. of 0·881 and an initial boiling point in the neighbourhood of 178° C. It is interesting to compare these figures with those given by Engler for decahydronaphthalene, sp. gr. at 0° C., 0·893, corresponding to 0·881 at 60° F., boiling point, 187°–188° C. He also states that the odour is "terpentinartig." Saturated hydrocarbons of this nature have been identified by Jennings in Louisiana crude oil (1906), and by Ross and Leather in a crude oil from Borneo (1906). Mr. Wilson stated that a fraction from this oil constituted a suitable white spirit, owing to its property of drying more rapidly than other oils of the same boiling point, and it is interesting to note that decahydronaphthalene is being manufactured by the hydrogenation of naphthalene and being used very successfully for this same purpose.

Mr. Dewhurst had raised a point with regard to the age of the oil. It would be of interest if the author could state if there was any reference in the literature of the subject which would throw any light on the age of the field from which the Badarpur crude oil was obtained. It appeared to him that oil of a composition as that described might be very much younger geologically than the oils of Burmah, Persia and some of the American oils. Another interesting point he wished to mention with regard to the Badarpur crude oil was that Mr. Robertson and himself had examined several oils from various wells in this field, and it was found that one in particular varied considerably from the others. That particular well, as far as he could remember, was a trifle over 800 ft. in depth, somewhat deeper than the others, the oil-sand being at a lower horizon. The oil coming from this well contained a very much larger percentage of lighter hydrocarbons, which to a very large extent were benzenoid. The fractions boiling between 130°/135° C. and 135°/140° C. were treated with nitrating acid and a crystalline nitro-compound resulted, which after recrystallisation melted at 97/98° C., corresponding to a mixture of 2, 3- and 2, 6-dinitro-paraxylene which melts at 99° C. Confirmation of this was obtained by nitrating to the 2, 3, 6-trinitroparaxylene, the resulting solid melting at 137°/138° C. It was considered particularly interesting to find that the predominant xylene present in this oil was the *para* compound, it being generally understood that the *meta* compound occurs more extensively in nature.

A further point worthy of observation is that during the process of fractionation of this oil a considerable amount of " autoxidation " took place. The residue left in the flask over night invariably darkened in colour, and there was on almost every occasion a separation of " water " from the oil, even when the fractionation was proceeding between 150° and 200° C. This rather points to the instability of this oil, and may suggest a road by which it may be investigated to commercial profit.

Dr. F. B. Thole, in reply to Mr. Esling's suggestion that the hydrocarbons analysed might be decahydronaphthalene and its homologues and not dicycloparaffins, pointed out that this possibility had naturally been considered but was quite untenable in view of the boiling points and molecular weights of the hydrocarbons isolated. Decahydronaphthalene ($C_{10}H_{18}$) boils at 184° C., while the hydrocarbon in this oil boiling at 175° C. has the formula $C_{12}H_{22}$, *i.e.*, its molecular weight is 20 per cent. higher than that of decahydronaphthalene. Moreover, the odour is entirely different to that of the latter hydrocarbon. If, as Mr. Esling suggested, the compound $C_{12}H_{22}$ were a dimethyldecahydronaphthalene its boiling point would be in the neighbourhood of 235° C., whereas it was actually 175° C.

Mr. W. J. Wilson, in reply, said that he was sorry he had not any quantitative figures to offer to Dr. Dunstan relating to the ash content of the crude oils under discussion. The business of a commercial Research Department left very little time for work which appeared to be entirely of academic interest. If, however, an opportunity ever occurred of obtaining such quantitative results he would communicate them. He could not throw any light upon the different result obtained by Ramsey, but it was not surprising if an occasional sample varies considerably from the average. His own analysis certainly showed only a very small trace of nickel, and it was difficult to see how there could be any room for error in that connection. The same remark applied also to the trace of cadmium. That was examined with care, and there did not seem to be any possibility of its having been confused with arsenic, especially as the latter element would probably have volatilised at the temperature at which the ash had been ignited. The quantity of cadmium, however, was very small. He could readily confirm Mr. Allan's remarks with regard to the value of the atmospheric apparatus for producing automatically blended distillates. Any kind of fractional distillation, whether conducted over a column or roughly from a distillation flask, gave such a fractionation that the heavier petrol such as was required for the specification would not contain the necessary proportion of low boiling point hydrocarbons, and consequently blending was necessary. But the atmospheric plant, a model of which he had had the privilege of working with, certainly had the property of producing just such blendings as were required for commercial use. In reply to Mr. Cunningham-Craig, he was not able to obtain any information with regard to the differences of the oils from the different sands, but he knew that his colleague in Rangoon, Major Carpenter, was keenly interested in that matter, and was doing all that could be done to secure information of that kind which was obviously of so much interest. He believed the Twingon area was exhausted, and he had had no opportunity of examining the oil that had been produced there. Mr. Lomax's question with regard to the association of Digboi oil with water, and also that of Mr. Esling regarding the geological age of Badarpur crude oil had been answered by Mr. Dewhurst. Mr. Dewhurst's remarks concerning the possibility of the action of water on the Badarpur oil were of much interest. It was impossible to give a very definite opinion about that matter, but it was quite well known that water, particularly under conditions of heat, reacted with heavy oils and altered their character rather considerably. His colleagues and himself had found that that action was multiplied considerably in the presence of very small traces of foreign substances. The action was much greater than when ordinary reasonably pure water was concerned. So

that there was just a possibility that in part at least the remarkable character of Badarpur crude oil might be due to its long association with water.

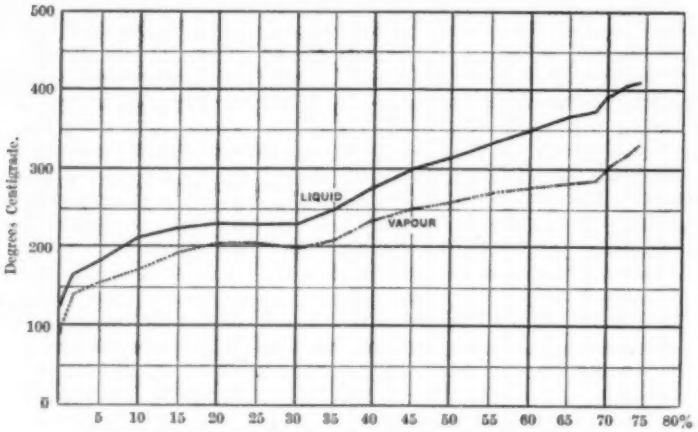
The President thought the Institution was to be congratulated on having had the opportunity of listening to such a valuable paper and the equally interesting discussion which had followed. The members were indebted to Mr. Wilson for presenting his paper, and he had very great pleasure in proposing a hearty vote of thanks to him for doing so.

The resolution of thanks was carried by acclamation, and the meeting terminated.

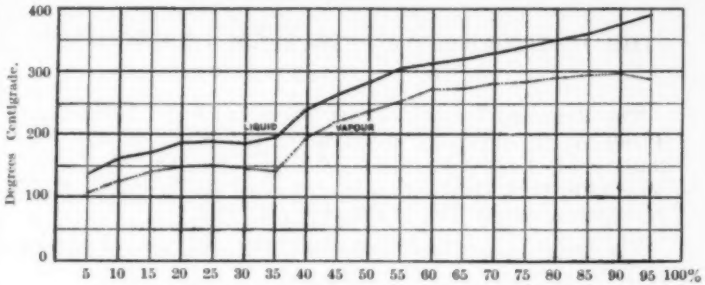
Mr. A. A. Ashworth subsequently wrote :—With reference to Mr. Wilson's paper on " Burma Crude," a point has arisen which I would like to submit. This point is in connection with the distillation temperature given on page 229. The point was not apparent until I had plotted the distillation curve on a graph, when it became apparent that from 20 per cent. off to 35 per cent. off the temperature of the liquid and vapour remained constant.

The extent of this irregularity is too great to permit it to be merely a personal variation in making the distillation, and there must therefore be some reason for it inherent in the crude oil itself.

On looking through my records, I found one similar case of variation in connection with the distillation of crude oil from Barbados, and my graphs of the distillation of both the Burma crude oil and the Barbados crude oil are appended.



DISTILLATION OF BARBADOS CRUDE OIL, SP. GR. 0·868.



DISTILLATION OF BURMAH CRUDE OIL, SP. GR. 0·835.

The only explanation of the above regularities that I can think of is that in both these oils distillates of constant boiling point are running off at the point indicated by the flat portion of the curve. Distillates of constant boiling point are rare in the distillation of crude oils and will probably only occur in cases of exceptional composition such as the large percentage of aromatic contents of the Burma crude and which may also be present in the Barbados crude but which I have not been able to prove owing to lack of laboratory accommodation.

In reply to the above, Mr. Wilson wrote :—The arrest of the rise of the temperatures of distillation (liquid and vapour) to which Mr. Ashworth draws attention is accounted for by the transition, mentioned in the description of the operation, from dry distillation to steam distillation. Steam being admitted after about 20 per cent. distillate is collected, the boiling point of the oil distilling necessarily falls slightly, and falls further as the quantity of steam is gradually increased. The externally applied heat is, of course, reduced as the steam distillation begins, and a certain degree of irregularity of the rate of distillation must also be allowed for in consideration of the distillation temperatures. Mr. Ashworth's graph shows a similar, though less pronounced, change in the gradient of the curves from the point at which distillation under reduced pressure begins.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE SEVENTY-NINTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, May 13th, 1924, the Chair being taken by the President, Mr. H. BARRINGER, M.Inst.C.E., M.I.Mech.E., M.I.N.A.

The Secretary first read the names of the newly elected members, as follows :—

Members.—Walter Henry Coleman, Charles Oswald Frewen Jenkin, William Henry Westwood Lacey, Richard Mannaberg, Ernest Procter, Charles Ross, Sir John Bowring Wimble.

Transferred from Associate Member.—Cyrus Henry Perkins.

Associate Members.—William Ernest Victor Abraham, Sidney Martin Blair, Bruce McLean Craig, Wyndham Percy Jones, George Martin Lees.

Students.—Leonard John Ward, Major William Wilson.

Associates.—William Robert Lincoln.

The following paper was then read :—

The Geology and Oil Measures of South-West Persia.

By R. K. RICHARDSON, A.R.C.Sc. (Member).

INTRODUCTORY.

The area forming the subject of this paper comprehends a long belt of petroliferous territory flanking the Persian Gulf on its eastern side and passing north-westwards through Arabistan and Bakhtiari Country into the Pusht-i-Kuh region of Luristan. It is bounded on the south-west by the desert lands of Persia and Mesopotamia, and on the north-east by the higher mountains of the Zagros arc.

Since Messrs. Mayo and Busk* delivered their paper before this Institution in 1918, much ground has been covered both in the field and laboratory. New regions and new rocks have come under the geological hammer, and much that was taken for granted, particularly in relation to the productive oil rock, has been the subject of revision.

* Some Notes on the Geology of the Persian Oilfields. *Journ. Inst. Petr. Techn*, V. No. 17, p. 3, 1918.

MAP OF S.W. PERSIA.

It can hardly be hoped, in the limits of this paper, to deal with the wealth of detail available, but it is proposed to review the geological features broadly and comprehensively, and the pertinent details of petroleum matters more particularly.

Before proceeding to the subject-matter the author desires to express his grateful thanks to colleagues of the Anglo-Persian Oil Company's Geological Staff, who have assisted in obtaining many of the data presented. Special reference will be made later to the valuable work of Dr. Douglas who has given much time and thought to the palaeontological determinations, and the author is indebted to him for the excellent illustrations of fossil forms.

Indebtedness must also be expressed to the Anglo-Persian Oil Company for having allowed the use of material from which this paper was compiled. In accordance with the rules of the Publication Committee of this Institution, the paper is written in the third person, but it should be clearly understood that the author accepts sole responsibility for opinions expressed and conclusions drawn, which may or may not be shared by colleagues or the Company.

Topographic Features.

Proceeding north-eastwards from the line of the Persian Gulf and the great rivers of Mesopotamia—heirs to an extended gulf in recent geological times—one traverses, in general, before reaching the central Iranian Plateau, a land mass of three-fold altitude. Firstly, a belt of alluvial desert at sea-level or thereabouts; secondly, a series of parallel hill ranges displaying the variegated colours of the Fars rocks and newer deposits; and, lastly, a series of high mountains formed by the Asmari limestone and rocks of older age.

The relief of the area has a N.W.–S.E. orientation, in keeping with its geological character, and is cut transversely by deeply-incised drainage lines across the strike carrying the waters of numerous rivers debouching into the Tigris, the Shatt-el-Arab and the Persian Gulf.

The relation of land forms to geology is an intimate one. The valleys are frequently broad structural valleys and the higher altitudes the crests of structural arches of massive limestone.

The long black hogbacks and whalebacks, representing almost intact arches of limestone, are a characteristic of the region. The two limestone groups, which function as the indurated framework of the country are the Asmari and the Cretaceous limestones.

In the sub-montane tracts occupied by later Miocene and Pliocene deposits conditions are often found reversed. Here the broad synclinal areas containing hard massive conglomerates of

BARD-I-QAMCHEH. GORGE. THE KARUN RIVER HAS HERE CUT ITS WAY THROUGH A BIG ANTICLINAL ARCH OF ASMARI LIMESTONE.

SMALL "TANG" IN ASMARI LIMESTONE ON THE SLOPES OF THE KUH-I-KAMERUN.

BAKHTIARI CONGLOMERATE. TANG-I-DOULAB.

UPPER AND MIDDLE FARS ROCKS. DAREH-I-QIL.

the Bakhtiari period form the higher country, standing out as extensive tablelands.

A striking feature of Persian topography is the presence of deep clefts or "tangs" in the limestone arches running transversely across the strike. The origin of these has been the subject of much discussion involving two alternative lines of enquiry. It has been considered that they are tectonic lines due to disruption by bending forces during orogenetic movements.

The alternative view ascribes their origin to erosion by rivers, keeping pace with uplift, during mountain formation.

They are identical with similar phenomena on a grander scale in the Himalayas for which the latter explanation is generally accepted.

Stratigraphy.

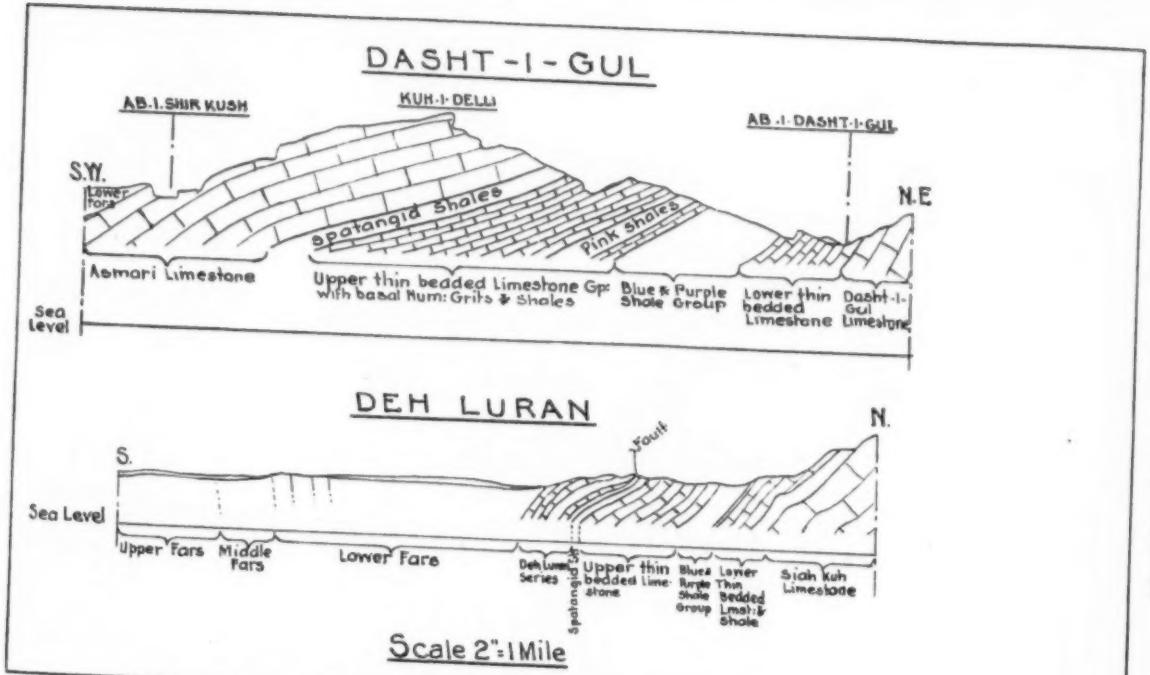
General.—Nature has facilitated geological enquiry in Persia in that she has laid bare, as on a dissecting table, the geological sequence stripped of superficial cover and disposed according to an order of grandeur and simplicity. It is fortunate that we have to deal with a succession in which individual members vary greatly in colour, hardness and other physical attributes.

While the sequence lends itself to divisibility into large and relatively simple units on lithological grounds alone, there is naturally some variation, particularly in thickness, from place to place. Considerable work has been done upon the Fars and newer rocks, but the older formations from the Asmari Limestone (Oligocene—Lower Miocene) to the Cretaceous had not, until recent years, been the object of close study.

The information about to be detailed relative to pre-Fars rocks rests upon three chosen sections, one in the North in the Deh Luran district of Pusht-i-Kuh, one in the centre typical of the oilfield region and Bakhtiari country generally, and one in the extreme South in the neighbourhood of Khamir, opposite Kishm Island in the Persian Gulf. These representative sections over widely separated areas, together with intermediate work, furnish stratigraphical scales from which a sound and general view of the geological sequence can be obtained.

For purposes of clarity and brevity it is proposed, with reference to pre-Fars rocks, to describe the central geological section in Bakhtiari country in detail, commenting on the others in passing. A glance at the correlation table will indicate their relations. Small overthrusts, glides, or crustal creep are largely responsible for a reduced thickness at Deh Luran.

In these general remarks on stratigraphy there is one point which should be made clear and that is, that when using European nomenclature to indicate age of respective groups, it must be



GEOLOGICAL SECTIONS DASHT-I-GUL AND DEH LURAN.

remembered that it applies in a general sense only. Europe is a long way from Persia and the geological periods of the latter, as represented by well defined rock groups, can only be expected to coincide roughly with European counterparts. If any system is to be made to fit the stratigraphical units of Persia the nomenclature and grouping of the Indian Geological Survey might in many respects be more suitable when modified to meet requirements.

Recent Deposits.—Deposits of high level gravels, silt and alluvial fans.

Bakhtiari Series.—This group, to which a Pliocene age is attributed, overlies the Fars Series unconformably. The discordance is strongly marked in some areas while in others it is less pronounced. The group consists of massive conglomerates, loose sands, and clays and has a maximum thickness of upwards of 15,000 ft.

The Fars Series.—The Fars Series covers many tens of thousands of square miles in Persia and largely occupies the submontane tracts of the region under consideration.

The relation between the basal, or gypseous group, of the Fars Series and the underlying Asmari Limestone has been given considerable attention. Overlap has been proved in some areas and in one or two rare instances unconformity is recorded. For the most part, however, over hundreds of miles of outcrop the junction has the appearance of being a conformable one. Detailed sections across the Maidan-i-Naftun oilfields show, however, a marked discordance between surface conditions and the Asmari Limestone, which is partly accounted for by overlap and proved lenticularity of deposits. It should be noted also that the junction of a hard, resistant limestone, such as the Asmari Limestone, with a soft gypseous series ready to become a semi-fluid under stress, provides ideal conditions for the development of slip planes and other phenomena which have possibly played their part during orogenetic movements.

The Fars Series has been divided into three sub-divisions, an upper arenaceous and red marl group, an arbitrary middle group, or passage series, combining the common features of the very distinctive upper and lower groups, and a lower gypseous series.

Upper Fars.—This is a sandstone and marl group several thousand feet in thickness of distinctive colour and appearance. The red tone of its outcrops and its general characteristics make it easily recognisable over immense distances with the naked eye.

The series consists of thick calcareous sandstones, red marls and shales, and a little veined gypsum.

Middle Fars.—This series is a passage group with arbitrary boundaries, and like most compromises it functions usefully while possessing many disadvantages. Its upper boundary is generally accepted as the first strong sandstone above which no bedded

gypsum occurs while its lower boundary is usually a sandy limestone marking the cessation of continuous bedded gypsum and indicating the close of the period of intense desiccation which characterised Lower Fars times.

The group comprises sandy detrital limestones, calcareous sandstones, blue and red shales and occasional beds of gypsum. It varies in thickness from a few hundred feet to 2500 ft. and more, according to the area and views of the observer.

Lower Fars.—The Lower Fars or gypseous group consists essentially of bedded gypsum with intercalated red and blue shales and marls, salt, anhydrite, and occasional beds of detrital and secondary limestones.

It varies in thickness from relatively small dimensions on old shore lines, contiguous with the older outcrops, to 5000 ft. and more in other areas, which may represent centres of great structural basins containing desiccative seas in Lower Fars times.

The salt and anhydrite are rarely met with in natural outcrops. This may be due in some measure to the solubility of the one resulting in concealment, and the liability of the other to change, by hydration, into gypsum. Evidence would indicate, however, that the salt and anhydrite are rather features of the lower horizons of the Lower Fars. They are invariably met with, sometimes in quantity, intercalated with gypsum and shales in drilling wells on the Maidan-i-Naftun oilfield and in remote outside tests areas.

The detrital limestones are an interesting group of rocks occurring as very occasional beds in the series. They are sporadic in development and when present show rapid lateral variation in thickness. Under the microscope they are shown to be composed of rounded and irregular worn grains of older limestones in a calcite matrix. Quartz grains are sometimes found in them also, and the size of the limestone grains varies very considerably in samples from different areas. The limestones have often undergone partial change by secondary methods to calcite and aragonite.

The Asmari Limestone Series.—The name Asmari Limestone is derived from Asmari Mountain, a long dark whaleback rising, as a barren and relatively unbroken limestone arch, to a height of 4500 ft. above sea level. The mountain which is a structural arch lies some twenty miles South-east of the Maidan-i-Naftun oilfield.

The Asmari Limestone Series is a uniform group of massive to thickly bedded, hard, compact, brown, or grey-brown limestone, frequently of great purity and displaying little evidence of being an oil container in its natural outcrops. Rare bands of hard calcareous shales appear towards the base of the group.

It is a series which is widespread in occurrence and maintains its individuality, with some variation in thickness, over enormous tracts of country.

In the Bakhtiari district it has an approximate thickness of 2000 ft. Specific measurements made show 1800 ft. at Dasht-i-Gul and 2200 ft. in the region of the Bard-i-Qamcheh gorge. In the Deh Luran district of Pusht-i-Kuh (where the names Deh Luran Series, and Kalhur Limestone, have also been applied) it is a little over 600 ft. in thickness but overthrust strike faulting has reduced the original dimensions. A feature of note in this area is the irregular replacement of part of the group by secondary gypsum. In some cases a thickness of 200–300 ft. of beds has been replaced in this manner. The change, which appears to take place from below upwards, gives rise to a dull white form of gypsum lacking the well stratified, compact appearance of Fars gypsum and containing undigested fragments of limestone. It may here be remarked that Prof. de Boetsh holds the view that the gypsum within the Asmari limestone is primary and represents an alternation of lagoon conditions with normal deposition of limestones during the Asmari period. In the Kazarun district, some 200 miles S.E. of the oilfields, the thickness approximates to that in the Bakhtiari region, while further South at Khamir, the Khamir Limestone, with which it is correlated, averages some 600 ft. in thickness. In the type area at Asmari Mountain only the upper 400 ft. of beds is exposed, while on the Maidan-i-Naftun oilfield the rock lies under a cover of impervious Lower Fars deposits varying in thickness according to the part of the field upon which drilling is undertaken.

The rock is highly organic, being a richly foraminiferal limestone in which the bulk of the remains are only revealed upon microscopic examination.

The Asmari Limestone has now been proved by petrographic, palæontological, and stratigraphical evidence to be the productive oil rock of the Maidan-i-Naftun oilfield.

Chemical analyses of samples from outcrops in various parts of Persia, and of samples of the oil rock from wells drilled on the oilfield, which reveal notable features on comparison, are dealt with in a subsequent section.

Spatangid Shales.—This is a small well-defined group yielding an Eocene fauna and underlying the Asmari Limestone conformably. It consists of bluish-green splintery shales containing occasional bands of compact, fine grained argillaceous limestone. The group has an approximate thickness of 250 ft., but varies in different areas. It is represented in the Khamir region by the Micropsis shales. (Upper Khamir argillaceous group.)

Upper Thin Bedded Limestones.—Underlying the Spatangid Shales conformably this group is composed of hard, fine-grained, thinly bedded limestone, greyish white to faint brown in colour.

The group contains thin shale bands and passes imperceptibly into the Spatangid Shales above.

In the Dasht-i-Gul region an arenaceous limestone and calcareous grit phase, with intercalated pink shales and conglomerate, is developed at the base of the group. A rich and varied fauna was collected from this lower development, including several varieties of Assilina, orthophragmina, and nummulites.

The group in the Dasht-i-Gul region, including the arenaceous phase at its base (600 ft.), has an approximate thickness of 1600 ft., while in the Deh Luran region it is 900 ft.

The Blue and Purple Shales.—This group, underlying the Upper Thin-Bedded Limestones conformably, is a uniform series of soft purple and blue shales, apparently non-fossiliferous.

A few thin limestone bands appear towards the summit, however, and these upon microscopic examination reveal orthophragmina and other Eocene forms. An approximate thickness of 1200 ft. was recorded. The group in general is probably Eo-Cretaceous in age—*i.e.*, Lower Eocene-Danian.

The Lower Thin-Bedded Limestones.—This group follows the above with apparent conformity. It consists essentially of white, hard, thin-bedded limestones, weathering cream to grey. Intercalated bands of fissile purplish-blue shales occur towards the summit. The group has an approximate thickness of 1200 ft. in the Dasht-i-Gul region.

A rich Upper Cretaceous fauna was collected from the top of the corresponding group in the Pusht-i-Kuh region at Deh Luran, where the thickness is 700 ft.

The Dasht-i-Gul or Siah Kuh Limestone.—The lowest beds examined by us in the Bakhtiari country comprise a group of hard, compact, fine grained, massive to thickly bedded limestones which are brownish grey on a fresh fracture. The group, Cretaceous in age, is of unknown thickness, as only a few hundreds of feet are exposed in the core of a faulted fold at Dasht-i-Gul. In the Deh Luran district (Siah Kuh Limestone) a thickness of 500 ft. was noted but the base was not seen. The Series, which makes important topographic features, is tentatively correlated with the Hippuritic Limestone in the South at Khamir.

Correlation.

The attached table, embracing geological sequences in successive areas, represents a broad tentative correlation over a large part of Persia.

The correlation table is based primarily upon lithological and stratigraphical evidence collected during the past few years, and

GENERAL CORRELATION TABLE.

is in the main supported by palæontological determinations. It will be noted that the distinctive units chosen have maintained their individuality over extensive areas with little variation except in thickness. There are one or two features to which attention might be drawn. The groups in the Bakhtiari country are all represented at Deh Luran but have diminished in thickness.

In the South the groups are maintained with some variation in thickness, and slight variation in character below the Eocene shales—*i.e.*, the Lower Khamir argillaceous series, a group of argillaceous limestones and shales, embraces the thin-bedded limestones and the purple and blue shales of the regions to the North.

Palæontology.

During the last few years extensive fossil collections have been obtained and submitted to Dr. Douglas for examination. All identifications were made by him, and the author is indebted to him for the substance of the accompanying tables, which are based on his work.

There are several points to which attention might be drawn. The Asmari limestone and its equivalents in other areas have been given an age Oligocene-Burdigalian. This is a compromise between Field evidence and palæontological results. The lower part is probably Oligocene and the upper part Lower Miocene. This ubiquitous massive limestone, which is everywhere underlain conformably by Eocene shales and overlaid by Lower Fars gypsum, has yielded a fauna more typically upper Oligocene (Num. Intermedia) in the South, and more typically Lower Miocene (Lepidocyclina beds) in the North. It would appear probable that the Lower Fars-Asmari Limestone junction is not a true time-plane throughout Persia.

Mingling of the significant members of the two faunas has been found in intermediate areas. Dr. Douglas has suggested that conditions of desiccation bringing in Lower Fars deposits may have proceeded from South to North slowly, which offers a tentative explanation of the conditions observed.

Examination of a large number of rock slides prepared from the Asmari limestone shows a regular distribution of forms. The basal beds are characterised by lepidocyclina, cycloclypeus and amphistegina; the intermediate beds, forming the bulk of the sequence, by alternating zones of Heterostengina and Asmaria,

LOWER FARS ROCKS WITH DETRITAL LIMESTONES. ANDAKAH.

LOWER FARS OVERLYING ASMARI LIMESTONE. DASHT-I-QIL. BIKARZ AREA.

DEH LURAN SERIES (ASMARI LIMESTONE SERIES). SHOWING GYPSEOUS PHASE.

ASMARI LIMESTONE (a) OVERLYING SPATANGID SHALES; (b) WITH UPPER BEDS OF UPPER THIN BEDDED LIMESTONES JUST EXPOSED; (c) BARD-I-QAMCHEH.

with alveolina and miliola; the upper beds with the alveolina-miliola fauna.*

The general ages of the groups are indicated in the attached tables :—

FOSSIL TABLE No. 1.

THE FOLLOWING FOSSILS HAVE BEEN FOUND IN THE FARS.

UPPER FARS. Upper Miocene.	Gasteropods abundant. Miliola sp. Polystomella sp.	
MIDDLE FARS. Middle Miocene.	Miliolina seminulum. " valvularis. " tricarinata. " linneiana. " alveoliniformis. " oblonga. " " Textularia agglutinans. " gibbosa. Spiroloculina excavata. " planulata. Lagena laevis. Globigerina conglobata. Polystomella craticulata.	Peneroplis carinatus. Pentellina chalmasi. Nodosaria cf. congobrina. " sp. Heterostegina depressa. Pecten (chlamys) multistriatus. Lithophagus lithophagus. Rotalia papillosa. Lamellibranch shells. Annelid tracks. Ostrea ?
LOWER FARS. Lower Miocene.	Ostrea cf. multicostata. " virleti. " sp. multicarinata. " sp. Bulimina orata. Globigerina bulloides. Sigmoilina orata. Sphaeroidina bulloides. cf. Pecten soomrowensis. Venus (clausinella) sp.	

* Asmaria is a new and enigmatical form very prevalent in the Asmari limestone. In spite of its well-defined characters, experts are undecided as to whether it belongs to the animal or the vegetable kingdom.

FOSSIL TABLE 3.

		DEH LURAN.	*DASHT-I-GUL.*	*BARD-I-QAMCHEH.*	*KHAMIR.* (U. Argillaceous series.)
		Approx. 120—500 ft.	Approx. 250 ft.	Approx. 250 ft.	Approx. 450 ft.
SPATANGID SHALES.	UPPER EOCENE.	cf. Balanophylla. Cardita aff. mutabilis. cf. Cyprina semilunaris. Globigerina bulloides. Pericosmus cf. nicaisei. Rotalia sp. Schizaster rimosus. Trochocyathus sp. Textularia sp. cf. Venus Gumberensis.		Ditremaster nux. Ditremaster (Hemiaster) forreatus. Spondylus cf. bifrons. Pericosmus. Schizaster.	Micropsis gagaria, Venustula.

	DEH LURAN.	DASHT-I-GUL.
	Approximately 600 ft.	Approximately 1800 ft.
ASMARI LIMESTONE SERIES. *OLIGOCENE TO BURDIGALIAN.*	*Macroscopic forms.* Arca aff. Burnesi, D'Arch. Cardita aff. Mutabilis. Cytherea aff. Incrassata. Echinolampas amplus, Fuchs. Echinolampas sp. Euspatangus cf. Rostratus, D'Arch. Ostrea pseudodigitalina, Fuchs. Pecten favrei, D'Arch. Pecten cf. Augustus, Fuchs. Psammechinus coronalis Lambet. Scutella paulensis, Agassiz. Turritella angulata, J. de C. Sow. Venus aff. Gumberensis, D'Arch. *Microscopic forms.* Miliolina (Abundant) Amphistegina cf. Hauerina D'Orb. Operculina. Heterostegina. Textularia. Lithothamnium ramosissimum. Ceriopora anomala, Abich.	*Macroscopic forms*—2-300 *ft. from sur* Flabellipecten expansus, Sowerby. Conus cf. antiqus, Lam. & ponderosus. Natica sp. Calliostoma (trochus) sp. *Microscopic forms.* *Upper Asmari Beds.* Miliolina cf. valvularis, Reuss. Pentellina sp. Spiroloculina sp. Nubecularia sp. Peneroplis sp. Textularia sp. Rotalia sp. Orbiculina adunca, Fichtel & Moll. *Upper Middle Asmari Beds* (approx.). Miliolids (isolated). Rotalia-like forms. *Middle Asmari Beds* (approx.). Miliolina cf. triquetra, Brady. Planispirina cf. celata, Costa. Spiroculina sp. Lithothamnium. *Lower Middle Asmari Beds* (approx.). Lepidocyclina cf. dilatata Michelotti. Cycloclypeus. Amphistegina. Asmaria nom. nov. *Lower Asmari Beds* (lowest 200 ft. appr Lepidocyclina sp. (abundant). Operculina sp. Heterostegina ? Globigerina. Polyzoa.

...I-GUL.	MAIDAN-I-NAFTUN.	ASMARI MOUN
...ly 1800 ft.	Only 400 ft. tested by drill.	Only 400 ft. exp
...00 *ft. from summit* ...s, Sowerby. ... & ponderosus. ...p. ... Reuss. ...htel & Moll. ...*Beds* (approx.).	Alveolina cf. Melo, Fichtel & Moll. Alveolina cf. Ovulum Stache. Miliolina alveoliniformis, Brady. Miliolina seminulum, Zinne. Miliolina auberiana, D'Orb. Miliolina valvularis. Nonionina. Orbiculina ? Orbitolites ? Peneroplis. Polystomella. Rotalia. Textularia. Echinoid fragments.	Alveolina cf. Melo, Fichtel & Miliolina valvularis. Miliolina alveoliniformis, Bra Miliolina cf. triquetra. Textularia. Orbiculina. Nubecularia. Truncatulina. Planispirina celata costa. Polystomella. Reophax. Carpentaria. Asmaria, nom. nov. Lithothamnium. Echinoid fragments.
...pprox.). ... Brady. ... Costa.		
...*Beds* (approx.). ...ata Michelotti.		
...west 200 ft. approx.). ...ndant). ...stegina ?		

FOSSIL TABLE 2.

...ARI MOUNTAIN.		BARD-I-QAMCHEH.	KUH-I-DIRA.	KHAMIR.
...ly 400 ft. exposed.		Approximately 2200 ft.	Approximately 1700 ft. exposed.	Approximately 600 ft.
...elo, Fichtel & Moll ...laris. ...niformis, Brady. ...quetra.	Occur frequently	Alveolina cf. Melo. Heterostegina. Asmaria, nom. nov. Miliolids (abundant).	Alveolina. Miliolina alveoliniformis. Miliolina auberiana. Miliolina valvularis.	Astrocoenia ramosa Sow. Carpenteria. Echinolampas cf. tumidopetalum, Gregory. Euspatangus cf. Formosus, de Loriol.
...ata costa.	occasional.	Amphistegina hauerina, D'Orb. Globigerina. Peneroplis. Polystomella. Textularia. Sphaeroidina. Nonionina. Ceriopora anomala.	Peneroplis. Polystomella craticulata. Rotalia papillosa. Textularia trochus, D'Orb. Sphaeroidina bulloides, D'Orb. Nubecularia lucifuga, Defr. Sigmoilina. Pentellina. Operculina (Heterostegina).	Exogyra persica sp. nov. Fistulana cf. egyptica, Opp. Globigerina. Isastraea cf. irregularis, Duncan. Lithodomus sp. cf. Verbecki, Boettger. Lithothamnium sp. Miliola seminulum. Miliola sp. Nummulites intermedia, D'Arch. Nummulites fichtelis, Mich. Nummulites garansensis, Leym. Nubecularia Boliviana.
...nov. ... ...ents.	At lowest horizon exposed.	Rotalia. Lithothamnium ramosissimum. Nubecularia. Discorbina. Truncatulina. Miogypsina cf. Burdigalensis, Gumbel. Echinoderm fragments. Lepidocyclina dilatata var. elephantina. Lepidocyclina dilatata, Michelotti. Lepidocyclina raulini, Lam & Douv. Amphistegina lessoni D'Arch. Cycloclypeus. Tinoporus. Pulvinulina.	Carpenteria proteiformis, Goes. Amphistegina lessonii, D'Orb. Lepidocyclina dilatata, Lem. & Douv (?) Nummulites intermedia, D'Arch. Lithothamnium. Echinoid fragments. "Cruciformis" nom. nov.	Nubecularia sp. Orbicella cf. Haimei, Abich. Ostrea cf. digitalina, Eich. Pachyseris murchisoni, Naime. Phyllangia alveolaris. Polystomella craticulata. Pentellina sp. Pecten cf. Labadyei, D'Arch. Pleurotomaria sp. Phasianella sp. Spines cf. Cidaris. Trochus cumulans. Turritella cf. Affinis D'Arch.

Fossil Table 4.

KHAMIR.

FOSSIL TABLE 4.

	DEH LURAN.	*DASHT-I-GUL.*	*BARD-I-QAMCHEH.*	*KHAMIR.* (Very argillaceous in this district.)
	Approx. 900 ft.	Approx. 1500 ft.	Less than 100 ft. exposed.	Approx. 1400-1500 ft. including Blue and Purple Shales.
UPPER THIN BEDDED LIMESTONE GROUP. MIDDLE EOCENE.	Pericosmus sp. Schizaster sp. cf. rimosus.	(From basal grits). Assilina exponens. ,, mamillata. ,, spira. ,, granulosa. Alveolina ovoidea. ,, irregularis (nov). ,, bulloides. Globigerina. Miliola cf. valvularis. ,, cf. biloculina. Miliolina alveoliniformis. Lithothamnium sp. Nonionina sp. Nummulites gallensis. ,, uroniensis. ,, laevigatus. ,, scabra. ,, guettardi. Orthophragmina cf. umbilicata. Orthophragmina cf. nummulitica. Orbitolites sp. Pentellina sp. Rotalia sp. Textularia sp.	Algae (?) cf. Chondrites. Annelid tracks. Ditremaster nux. Pecten (chlamys) subdiscors. Pericosmus.	Alveolina ovoidea. Nummilites Biarritzensis. Orthophragmina Umbilicata. Globigerina sp. NOTE.—Upper thin bedded limestones and blue and purple shales are classed as one group in this region.

Fossil Table 5.

	DEH LURAN.	*DASHT-I-GUL.*	*KHAMIR.* (Lower Argillaceous Series.)
	410 ft.	1200 ft.	1400-1500 ft. including upper thin bedded limestones.
BLUE AND PURPLE SHADE GROUP. LOWER EOCENE. TO DANIAN.		Found in upper beds. Orthophragmina sp. Lithothamnium sp. Sphaeroidina dehiscens. Globigerina. Dentalium.	

Fossil Table 6.

	DEH LURAN.	*DASHT-I-GUL.*	*KHAMIR.*

FOSSIL TABLE 6.

LOWER THIN BEDDED LIMESTONES (SENONIAN).

DEH LURAN.	DASHT-I-GUL.	KHAMIR.
700 ft.	1200 ft.	
Baculites sp.	Globigerina.	
Campanile.		
Cardium.		
cf. Echinoconus Carcharias.		
Goniopygus superbus.		
,, cf. durandi.		
Hemipedina neemiae.		
Holectypus cf. inflatus.		
Hemiaster neomiae.		
,, iranicus.		
Iraniaster cf. Douville.		
,, Morgani.		
Membranipora sp.		
Natica sp.		
Ostrea (Lopha) Dichotoma.		
,, ,, ,, var Persica.		
,, ,, ,, ,, Rotunda (nov)		
,, ,, sollier.		
,, (Pycnodonta) vesicularis.		
,, curvirostris.		
Orthopsis Morgani.		
Parapygus cf. inflatus.		
Pyrina orientalis.		
cf. Peterocera ornata.		
,, ,, supercretacea.		
Pecten (Neithea) striatocostata.		
Pseudocatopygus longior.		
Pygurostoma Morgani.		
Plicatula hirsuta.		
Pleurotomaria cf. perspectiva.		
Spondylus subseratus.		
Salenia cossiaca.		
Terebratula Brossardi.		
,, toucasi.		
Tricephalopora sp.		

FOSSIL TABLE 7.

	DEH LURAN.	*DASHT-I-GUL.*	*KHAMIR.* (Hippuritic Lst.)
	500 ft. exposed.	200-300 ft. exposed.	1200 ft.
SIAH KUH LIMESTONE.	Nerinea cf. marrotiana. Radiolites. Trochosmilia compressa.	NO FOSSILS FOUND.	Caprinella doublieri (?) Durania laevis (?) " Mortoni (?) Sauvagesia praesharpei (?) " nicaisei (?) " Da Rio (?) (The Persian Hippurites are unusually large and many may be entirely new to science.)

Geological History and Tectonics.

Persia is pre-eminently a country of fold mountains. The grain of the country is north-west to south-east, and the fold lines and overthrust faults invariably have this orientation.

The Zagros arc and its associated ranges in Persia form part of a southern loop of the Great Alpine Himalayan belt which passes across Europe and Asia, and it is to this period of mountain building—the great Himalayan upheaval, in Tertiary times, that the system of folded structures and faults are due.

In considering the geological sequence, the absence of stratigraphical discordance over long geological periods, postulating continuous deposition and a period of relative quiescence from Senonian, to the end of Asmari times, is noted.

At the end of the Asmari period it is presumed the forces of upheaval manifested themselves and initiated the lines of subsequent elevation. The movement was obviously not very profound, but was sufficient to cause overlap and slight discordance between the Asmari limestone and the succeeding Fars deposits. At this period also climatic changes of a far-reaching character came into operation, resulting in a period of intense desiccation, during which the chemical deposits, salt, gypsum and anhydrite, of the lower Fars period were laid down. The order of deposition in a drying sea is considered to be gypsum, salt, other sulphates, other chlorides. It is understood that chemical proof is available that anhydrite instead of gypsum can be deposited in the presence of magnesium salts. Evidence of magnesium salts is abundant in analyses of water from Lower Fars rocks. Any disturbance of the salinity of the seas such as would be brought about by alternating periods of rainfall would cause an alternation of the salts in order of deposition, such periods of rainfall would also bring down sediments from which marls and clays would be formed. In areas sufficiently near to limestone masses, beds of detrital limestone would be laid down.

In the Maidan-i-Naftun oilfield the oil-bearing Asmari limestone is usually overlain by a zone of anhydrite ; this is succeeded by a zone of intercalations of salt, gypsum, rare anhydrite and shales. The salt zone is succeeded by further bedded gypsum, intercalcated red and blue shales and occasional detrital limestones.

The close of the period of desiccation is marked by the cessation of continuous bedded gypsum and the incoming of numerous detrital limestones, calcareous sandstones, and shales, with rare gypsum beds, of the Middle Fars sequence.

The Middle Fars is succeeded imperceptibly by the coarser, non-gypseous group of sandstones and marls of the Upper Fars period.

The history of Fars times is thus the gentle inception of the folding movement, a period of intense desiccation relieved at the end of Lower Fars times and followed by normal depositional conditions.

Of the boundaries of these desiccated inland seas of Lower Fars times little is known as geological investigations have not been carried sufficiently far afield. In South Persia, however, some fifty miles eastward of Bunder Abbas, at Minab, we have the Zindon Range which marks approximately the shore line of a Tertiary land surface to the east, and a Fars sea to the west. This ancient barrier of older rocks separated the highly saline Lower Fars seas in which a chemical series was laid down, from the more normal marine areas of Mekran and Persian Baluchistan where separate depositional conditions obtained.

Folding movements may have continued slightly during Fars times, but, on the whole, the period was one of relative quiescence compared with the gigantic upheaval which took place at the end of the period. The close of the Upper Fars period is marked by intense orogenetic movements. It is the second phase of the earlier movement which defined geological trend lines at the end of Asmari times. Regional uplift on a grander scale obtained. The fold lines were emphasised, drainage lines steepened and concurrently with this, the newly-formed mountains were subjected to violent degradation. The enormous thickness of torrential conglomerates of the Bakhtiari period, lying unconformably on Fars rocks, bears witness to the severity of the processes involved.

This movement was probably continuous during Bakhtiari times, though with less violence, giving rise to the phenomenon of continuous unconformity which the Bakhtiari sediments display.

In post-Bakhtiari times the third phase of the movement, and probably the most severe, was initiated, leaving the stratal disposition more or less as it is to be found to-day. In this movement the rocks of the Bakhtiari period participated.

Earth movement appears to have been from north-east to south-west. In the higher mountains to the north-east the folds are more severe; passing south-westwards to the lower mountains the limestone ranges have frequently a somewhat steeper south-west limb and a gentle north-east limb; coming to areas where the softer Fars rocks are more prevalent we find the north-east limbs gentle and normal, while the south-west limbs are over-thrust and frequently obscured by transferred sheets of the upper fault blocks. The gypsum of the Lower Fars under the stress of folding forces has flowed, as a plastic mass, over the south-west limbs of numerous folds, and has frequently been driven over the younger Bakhtiari masses spreading over them amoeboid fashion, along thrust planes, but little removed from the horizontal. A

SEQUENCE DISPLAYING PART OF DEH LURAN SERIES (GYPSEOUS PHASE); SPATANGID SHALES (IN VALLEY IN FOREGROUND); UPPER THIN BEDDED LIMESTONES AND SIAH KUH LIMESTONE.

NUMMULITIC FACIES OF UPPER THIN BEDDED LIMESTONES A—A′. DASHT-I-GUL

PURPLE AND BLUE SHALES. DASHT-I-GUL.

SIAH KUH LIMESTONE. PUSHT-I-KUH

traverse from the Persian Plateau, south-west, towards the plains shows the resulting structure clearly. Close folds are to be seen in the hard limestones of the north-east giving rise to gentler folds to the south-west. When the softer gypseous formations are reached the overthrust south-west limbs are manifested, while as we proceed further, even the softer rocks are less plicated until the gentle domes of such places as Kuh-i-Bang near Bushire indicate the last ripples of the spent forces.

Having dealt with the tectonics in general, a more detailed study of a particular area will follow when considering the structural features of the Maidan-i-Naftun oilfield.

In concluding this study of the geological history and tectonics of the region it may be mentioned certain structures characteristic of the southern part of the Persian Gulf. On Kishm Island, Henjam Island, Hormuz Island and other Gulf islands as well as on the Persian mainland in the region of Lingeh and Bunder Abbas, well-defined salt domes occur. The scope of this paper and the space available forbid more than a passing notice of these interesting structures.

The sequence of folding movements is shown in the following Table :—

Tabular representation of Geological movements.

3rd Phase of Himalayan upheaval.	Pleistocene and recent deposits.	Final grand upheaval at close of Bakhtiari Period.
	Bakhtiari Period. During which conglomerates and sands of non-marine origin were laid down under continued earth movement.	
2nd Phase of Himalayan upheaval.		Commencement of first big upheaval which continued throughout Bakhtiari times.
	Fars Period. A period of relative quiescence during which slight and gradual uplift—a continuation of the initial earth movement—may have occurred. Argillaceous deposits and chemical precipitates were laid down under conditions of intense desiccation relieved at the end when the older Fars rocks were laid down.	
1st Phase of Himalayan Movement.		Initiation of earth movement.
	Asmari Period. During which a great thickness of massive limestone was laid down.	

Origin of the Oil.

Oil indications in Persia characterise rocks of all geological ages from the pre-cretaceous to pliocene. They are probably most abundant in the clastic and secondary limestones of the Lower Fars, as at Maidan-i-Naftun and Naft Khaneh, and near the Lower Fars—Asmari boundary, as at Dasht-i-Qil. Near Malamir they occur in the Bakhtiari series, while in the Deh Luran-Dalpari region they characterise most of the rocks from the Lower Fars to the Siah Kuh limestone. At Imam Hassan they occur in cretaceous shales. At Dareh-i-Qil they occur near the Middle-Lower Fars junction, and near Champeh in the Persian Gulf they occur along the plane of intrusion of a saline plug.

They are usually found in limestones, though they have often been observed in gypsum, sandstones, conglomerates and shales.

The origin of the oil in Persia is a matter requiring careful deliberation. Evidence is gradually accumulating which will need analysing and marshalling; but, above all, premature judgment is to be avoided. There are two alternative views:—

(*a*) An indigenous origin in the Asmari limestone.

(*b*) A Cretaceous origin followed by migration into the Asmari limestone.

The Upper Fars has also been suggested as a source of origin, but this view has not at present much evidence in its favour.

Initially it would be unscientific to neglect to search for the origin of the oil in the rocks at present containing it, unless it can be proved that the reservoir rock is incapable of producing the necessary organic matter.

It must be stated that the Asmari limestone or its equivalent in other areas provides, together with overlying Fars limestones, the most abundant and the most prolific oil-shows in the country, and at Maidan-i-Naftun the Asmari limestone yields oil in enormous quantities. It is a highly organic rock composed almost entirely of foraminiferal remains, and bulk for bulk is uniformly far richer in organic matter than any other formation examined.

The Asmari limestone is underlain by a thick body of blue shales, which would function as an impervious series obstructing migration from below, and is overlain by an impervious cap of Lower Fars gypsum, shales and anhydrite.

The alternative view that the oil originated in Cretaceous shales is due a full examination. There are many difficulties, however, in the way of its acceptance.

If it is a matter of evidence of association, then the indigenous theory of origin in the Asmari limestone has much more in its favour. Apart from this, however, there are grave objections to

the theory on other grounds. If the oil of the Maidan-i-Naftun oilfield originated in Cretaceous rocks, by what means did it reach its present position? It has been suggested that the migration might have taken place along Tang lines, presumed super-fissures; but this view, against which much evidence is arrayed, is not generally accepted by geologists. There remains the method of direct upwards migration across the intervening sediments from Cretaceous shales to the Asmari Limestone. Difficulty is found in appreciating the *modus operandi* involved in this passage across some thousands of feet of thin-bedded limestones and shales, and we are entitled to ask, if this hypothesis is postulated, by what means the upward migration, through reputed impervious strata, was finally arrested in the rocks in which the oil is found at the present day? It is also anticipated that the oil in the Asmari Limestone would bear evidence as to its peregrinations, but in the many analyses of Persian oils no such evidence, so far as the author is aware, has been revealed.

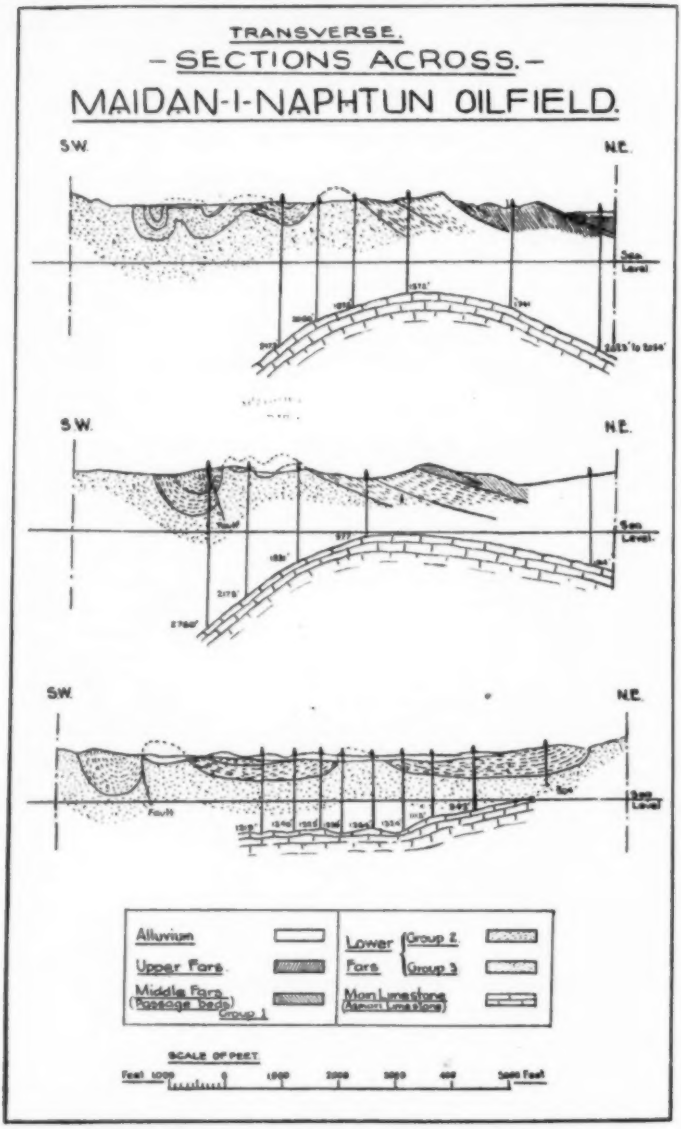
In postulating an indigenous origin for the oil in the Asmari Limestone at the Maidan-i-Naftun oilfield, the author does so without prejudice to the possibility of a Cretaceous origin for Cretaceous oil, and the chances of successful exploitation of such sources.

In the above the organic origin of the oil has been treated as axiomatic and the remarks have been chiefly concerned with this aspect and questions of migration. It may be stated, however, that if there is anything in the Limestone, gypsum, and hot water theory of the origin of petroleum, Persia offers a good field for study. For the benefit of supporters of this view it is noted that the Lower Fars limestones upon the oil field display secondary changes to calcite and aragonite. The presence of considerable aragonite, which postulates the action of heated water, is significant. Some of the author's colleagues have drawn attention to the striking association of these minerals with oil in other petroliferous areas in Persia.

The Maidan-i-Naftun Oilfield.

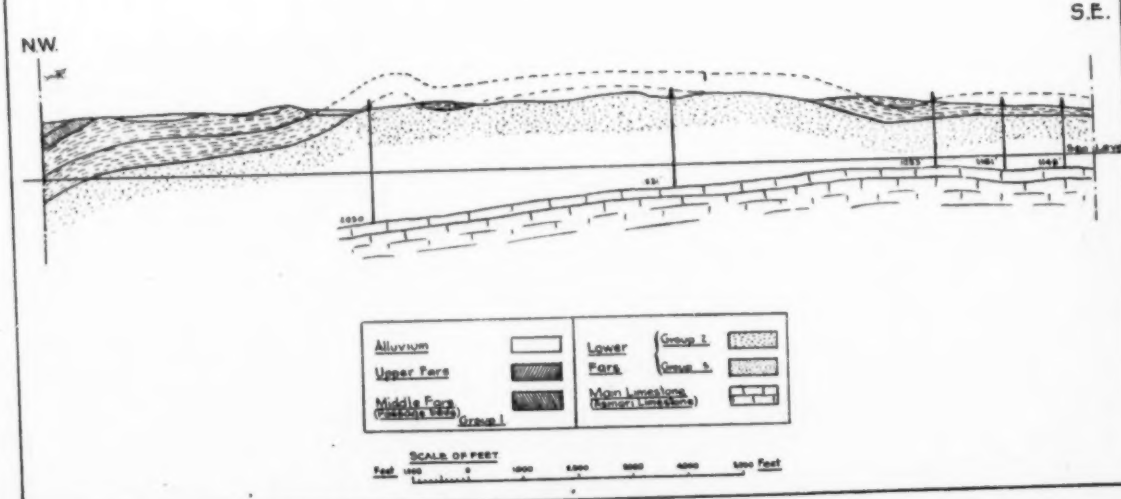
The richness and sustained production of this remarkable oilfield make it one of the most important of the world's petroleum resources. It is situated approximately 140 miles N.N.E. of the Port of Abadan, on the Shat-el-Arab, to which place oil is transported by pipe-line.

The boundaries of the productive area are being continually widened by prospect wells, but the extent of its untapped reserves is still unknown. Production figures, which have already been published, representing the volume of oil extracted from a rela-



TRANSVERSE SECTIONS ACROSS MAIDAN-I-NAFTUN OILFIELD.

LONGITUDINAL
— SECTION ACROSS. —
MAIDAN-I-NAPHTUN OILFIELD.



LONGITUDINAL SECTION ALONG MAIDAN-I-NAFTUN OILFIELD.

tively small number of wells, indicate the richness of the territory. These figures, however, are merely a measure of the progress of pipe-line, refinery and tanker construction, which afford at present the only limits to productivity :—

TOTAL ANNUAL PRODUCTION—MAIDAN-I-NAFTUN.

Year.	Crude Oil Gallons.	Equivalent Tons.
1912–13	21,896,714 ..	82,629
1913–14	74,155,141 ..	279,831
1914–15	101,889,665 ..	384,489
1915–16	121,785,808 ..	459,569
1916–17	174,544,131 ..	658,657
1917–18	243,196,050 ..	917,721
1918–19	293,199,729 ..	1,106,414
1919–20	367,104,918 ..	1,385,301
1920–21	468,693,795 ..	1,768,656
1921–22	625,066,465 ..	2,358,741
1922–23	788,209,802 ..	2,941,081

Geological Features of the Oilfield.—Previous reference has been made to the general simplicity of the stratigraphic succession and the bold fold lines of the country. While this statement of first principles remains valid a detailed study of any particular area in Fars rocks, in relation to petroleum exploitation, involves the application of all the aids to geological inquiry.

The Maidan-i-Naftun Oilfield comprehends an anticlinal area in Fars rocks with a general axis running N.W.—S.E. Over the main area of the fold the Lower Fars or gypseous series is exposed. The North-Eastern flank of the anticline is relatively gentle, while the South-Western flank is completely obscured by an overthrust, the Tembi fault. The Lower Fars gypsum has been driven over the steep limb in the manner indicated in our study of tectonics.

It is one of the many anticlinal areas in Bakhtiari country displaying similar superficial characters in regard to stratigraphy and structure, but which lack the abundant oil scepages characterising the Maidan-i-Naftun area.

The main anticline is affected by a complicated system of minor folds. A glance at the detailed sections across the field will make this clear. These minor structures are open and simple in the central part of the area where they lie in relative proximity to the solid resistant Asmari mass below. To the South-West they become more compressed until both limbs achieve verticality. A zone of isoclinal and recumbent folds, with minor reversed faults follows, until the main thrust, the Tembi fault, is reached. The axes of these minor folds in the isoclinal region conform with the general strike line of the main anticline, but in the more openly folded, central part of the area they are often tortuous.

These plications of the Lower Fars series, which are probably the result of folding forces acting upon a soft and non-resistant series, are not reflected in the rigid Asmari massif below.

The view has been put forward that the minor folds may be due to a conversion of anhydrite to gypsum. The hydration of anhydrite involving an expansion, variously estimated at 25—50 per cent., would be capable of considerable local effects. The theory would, however, postulate that a large quantity, if not all, the Lower Fars gypsum was originally deposited as anhydrite. A zone of anhydrite is found overlying the main limestone in most wells, but its presence appears to be independent of distance from a possible zone of weathering. It is found both in shallow and in deep wells. While the possibility of chemical change from anhydrite to gypsum, resulting in local structures, cannot be denied, it is considered that the crumpling forces of post-Bakhtiari earth movements offer an explanation more acceptable, and more in accord with the general geological features of the problem.

The Lower Fars series overlies a broad Asmari massif of anticlinal character. Drilling results indicate that it has a gentle North-East flank and a slightly steeper South-West flank. It also pitches gently to the North-West.

A discordance between surface features in Fars rocks and the underlying Asmari limestone is clearly shown in the sections. It has the appearance of strong unconformity, but this view is misleading. Throughout Bakhtiari country the junction between the two groups at outcrop is a conformable one, and conformity with overlap probably represents the true relation of the groups. The effect of unconformity is due partly to minor folding in which the Asmari limestone has not shared. It is also partly due to proved lenticularity and to overlap of deposits. The nature of the junction—a soft gypseous series with a limestone mass—also offers excellent facilities for the development of slip planes during folding. Mr. H. G. Busk has recently put forward the view, with supporting evidence, that the junction is a slip or thrust of this character, a view that deserves the fullest consideration.

The Asmari limestone is met by the drill in most wells at depths from 1000—3000 ft., according to their positions relative to the anticlinal Asmari mass below. Indicators of the approach to the oil rock are usually slight gas or oil, and the presence of white powdered anhydrite in the drilling samples.

The Productive Oil Rock.—There are copious oil seepages on the Maidan-i-Naftun oilfield which almost invariably exude from the detrital limestones of the gypseous series. Oil shows are also found in Fars rocks above this horizon.

The detrital limestones of the Lower Fars series were for many years considered to be the productive oil rocks of the field. Inves-

tigation, however, during the last few years has conclusively proved that this is not the case. The microscope has revealed the oil rock to be, not a detrital limestone, but a highly foraminiferal rock of non-clastic character identical with the rock at Asmari Mountain. Stratigraphical knowledge, and drilling evidence, moreover, disallow the postulation of any other view. The supersession of the detrital limestone theory and the proof that the productive oil rock is the Asmari limestone has changed the outlook of petroleum geology relative to the oilfield, and a very much larger productive area is assured than was formerly thought to be the case.

Dolomitisation.—The Asmari limestone, which has been noted under stratigraphy to be hard and compact in natural outcrops, has been rendered a porous reservoir rock by dolomitisation and other agencies.

Dolomitisation is the change by metasomatic processes of a limestone comprised mainly of calcium carbonate to a rock composed of calcium magnesium carbonate. The change, theoretically, involves a reduction in volume of over 12 per cent. and a fissured, cavernous, or loose rubbly structure is a frequent result of the process. It is generally regarded that magnesium chloride is the active substance in solution which establishes this change, and even in our present-day analyses of Lower Fars waters from wells a high magnesium chloride content is registered.

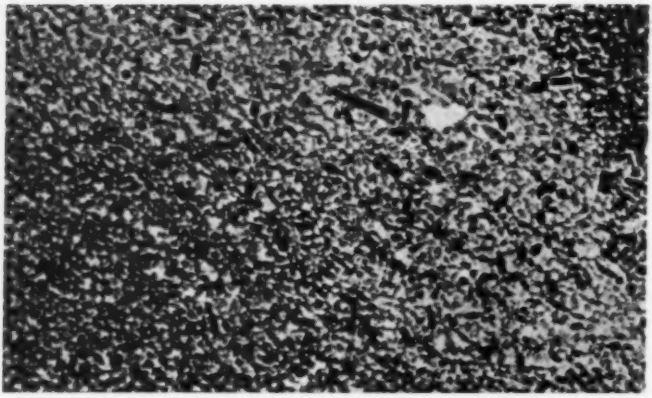
Dolomitisation has affected the Asmari limestone from end to end of the field, as the analytical tables will show. In the region of the Central Maidan at Naftun the rock is a pure dolomite, the magnesium and calcium constituents being present in almost correct molecular proportions. Other analyses show dolomitisation in varying degrees, but it yet remains to be seen whether the degree of dolomitisation will prove a measure of productivity in any particular well, as has been claimed in some American fields where a limestone reservoir obtains.

The author is indebted to Professor Hugo de Böckh for a valuable discussion on the subject of the dolomitic and cavernous nature of the Asmari limestone. He has indicated the probability that under the lagoon conditions obtaining at the end of the Asmari period the limestone was attacked by magnesium chloride and magnesium sulphate in solution resulting, by complex processes, involving the leaching out of calcium carbonate, in the formation of the cavernous dolomite termed "Rauchwacke," which is frequently associated with gypsum and salt formations. The resulting dolomite, it is claimed, apart from any porosity induced by dolomitisation alone, is thereby rendered highly porous, or even cavernous, by the changes involved.

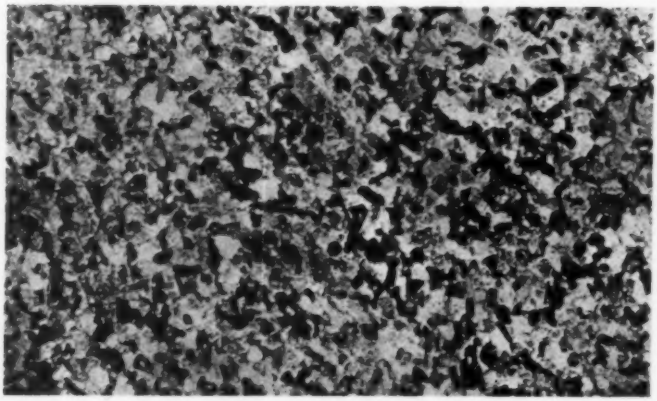
The following tables display analyses of the Asmari limestone

HIPPURITIC LIMESTONE (RIGHT). KHAMIR.

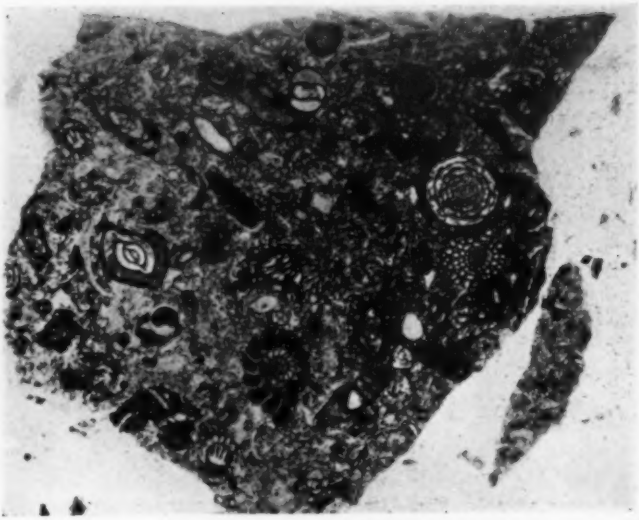
SALINE PLUG OF HORMUZ SERIES (LEFT) INTRUDED THROUGH UPPER FARS (RIGHT). NAMAKDAN, KISHM ISLAND



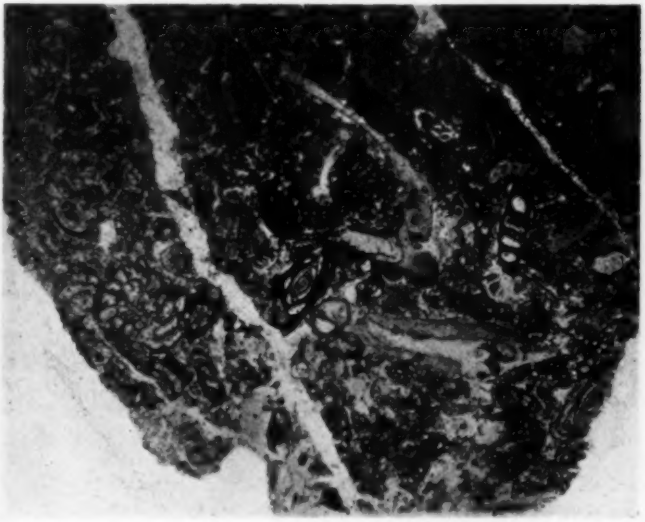
PHOTOMICROGRAPH OF DETRITAL LIMESTONE. LOWER FARS SERIES. MAIDAN-I-NAFTUN.



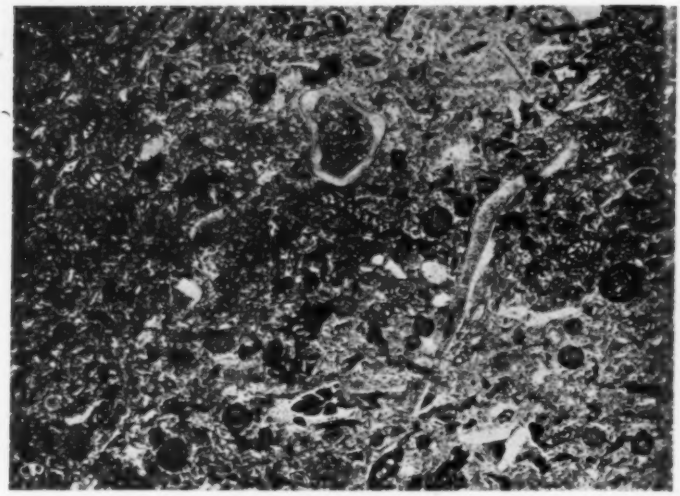
PHOTOMICROGRAPH OF SANDY DETRITAL LIMESTONE. LOWER FARS SERIES. DAREH-I-QIL.



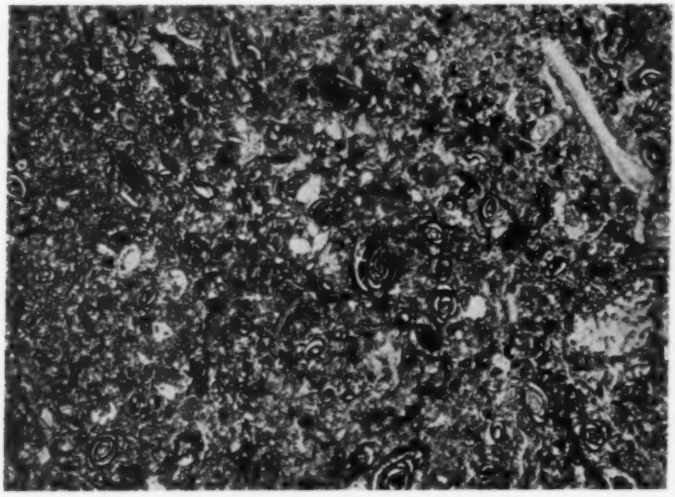
PHOTOMICROGRAPH OF OIL ROCK (ASMARI LIMESTONE). MAIDAN-I-NAFTUN. DISPLAYING ALVEOLINA CF. MELO AND MILIOLINE FORMS, ETC.



PHOTOMICROGRAPH OF OIL ROCK (ASMARI LIMESTONE). MAIDAN-I-NAFTUN. DISPLAYING MILIOLINE FORMS, ETC.



PHOTOMICROGRAPH OF ASMARI LIMESTONE ; UPPER BEDS. ASMARI MOUNTAIN. DISPLAYING ALVEOLINA CF. MELO, MILIOLINE FORMS, TEXTULARIA, ASMARIA, ETC.



PHOTOMICROGRAPH OF ASMARI LIMESTONE. UPPER BEDS. DASHT-I-GUL. DISPLAYING MILIOLA CF. VALVULARIS, TEXTULARIA, PENEROPLIS, PENTELLINA, ORBICULINA, ADUNCA, ETC.

made at outcrop, for comparison with analyses of the oil-bearing Asmari limestone at Maidan-i-Naftun. It may be mentioned here that some analyses of the Asmari limestone at outcrop, from the Bikarz area, where samples were collected in the vicinity of extensive oil seepages were, unlike those in the first table, highly dolomitic.

ANALYTICAL TABLES.—1.

Analysis of four samples of the Asmari Limestone from Outcrops.

	Asmari Mountain.		Bard-i-Qamcheh.	
	1.	2.	3.	4.
	%	%	%	%
Moisture	·05	3·74	·06	·12
Silica	4·21	2·70	4·19	3·19
Iron and Aluminium	·64	2·75	3·88	1·19
Calcium Sulphate	—	·42	1·53	·53
Calcium Carbonate	93·35	87·28	88·11	94·36
Magnesium Carbonate	1·72	3.54	2·27	·19

ANALYTICAL TABLES.—2.

Analyses of samples of the oil-bearing Asmari Limestone.

	Maidan-i-Naftun (8 Wells).			
	1.	2.	3.	4.
	%	%	%	%
Moisture	·73	·51	·40	·54
Bituminous Matter	1·46	·40	·79	·66
Silica	4·83	3·95	3.34	4·85
Iron and Aluminium	2.22	2·85	1·55	2·94
Manganese	·83	·66	·27	1·37
Calcium Sulphate	·34	1·33	1·15	1·42
Calcium Carbonate	48·94	49·09	49·97	47·90
Magnesium Carbonate	40·65	41·21	42·52	40·32
	5.	6.	7.	8.
	%	%	%	%
Moisture and Organic Matter	·98	·41	·60	4·55
Silica	3·58	5·75	2·90	8·49
Iron and Aluminium	1·80	2·68	1·40	2·85
Manganese	·19	·12	—	—
Calcium Sulphate	5·41	16·86	3·40	19·96
Calcium Carbonate	50·86	43·71	79·50	42·72
Magnesium Carbonate	37·15	30·34	12·20	21·43

In one particular well a series of four analyses were made from drilling samples of the oil rock selected at different depths. They revealed a decrease in the dolomitic content from above downwards.

In concluding this study of the Oil-Field region it may be stated that the Maidan-i-Naftun area has never been troubled by water, it has never registered a dry hole, and the limits of the productive area have nowhere yet been proved, though a continuous policy of marginal extension by test wells has been in operation for several years.

DISCUSSION.

The President said he was sure the members would agree that they had listened to a very interesting paper full of valuable information set out in an exceedingly clear manner, and he had no doubt it would lead to a valuable discussion. The question of the origin of petroleum was touched upon, and looking at the list of fossils and the micro-photographs it appeared to him that they might have some bearing on that subject.

Dr. Hugo de Böckh, in opening the discussion, said that it had not been his intention to speak, as he was only a visitor, but, having been asked, there were one or two comments which he wished to make. The paper touched on many scientific questions, but to discuss them all would take far too much time. It had recently been his privilege to spend some time in Persia, and he saw there a very characteristic feature. In Persia, a Miocene reservoir rock, containing great quantities of hydrocarbons, is overlain by the Lower and Middle Fars Series which contain gypsum and also, in addition, some hydrocarbons.

Hoppe-Seyler has demonstrated the following reaction:—

$$CaSO_4 + CH_4 = CaCO_3 + H_2S + H_2O.$$

If pulverised gypsum is put into a tube and methane passed through it, a gas is obtained which already contains H_2S. In this way gypsum is a very changeable rock.

If folding, faulting, or erosion open up the way for hydrocarbons they will come in contact with and change the gypsum. H_2S, on becoming partially oxidised, gives off native sulphur. In the pluvial period of the Diluvium there was much water and strong erosion.

The escaping gases agitated the water which contained sulphates, amongst them magnesium sulphate.

Complicated interaction set in, resulting in the various rocks of so-called "secondary action."

Mr. Richardson has referred to aragonite occurrences. It has been pointed out that all the waters of the Lower Fars contain magnesium sulphate. Having magnesium sulphate in solution and a temperature exceeding 29° C., aragonite, and not calcite, is deposited. In most other countries the deposits which are overlying and containing rocks saturated with hydrocarbons do not contain as much gypsum as those in Persia, so that there is no possibility of such interactions taking place.

Hydrocarbons do not attack clays, marls, or sandstones, and, according to the prevailing conditions, we get mud volcanoes, gas shows, oil shows, H_2S, and native sulphur. In Persia we find

"secondary action" resulting in different types of sinter deposits. It can be observed clearly how these sinter deposits are principally confined to diluvial terraces formed during the pluvial period. Of course, the waters circulating in the rocks would contain, more or less, H_2S, which could act on $CaCO_3$. Calcium hydrosulphide would be formed, and calcite, gypsum, and sulphur are then deposited.

Another question which was touched upon by Mr. Richardson is the porosity of the dolomitised Main Limestone. This porosity is due not so much to dolomitisation itself as to the leaching out of $CaCO_3$ during dolomitisation, or, in certain cases, at a later stage. It is often said that dolomitisation results in a porous rock, owing to the fact that by taking two molecules of $CaCO_3$ and replacing one molecule by $MgCO_3$ we obtain the double salt dolomite, $CaMg(CO_3)_2$, which will occupy as much space as one $CaCO_3$ molecule plus one $MgCO_3$ molecule. This would mean 12·2 per cent. less space. In this calculation the hexagonal modification of $CaCO_3$—calcite—is taken, but we have the more unstable modification of $CaCO_3$—aragonite—forming the shells of some animals. As aragonite has a greater specific gravity, the "shrinkage" would be only a half. Moreover, we know of dolomites—dolomitised limestones—which are quite dense rocks, and it must be pointed out that in the Alps and Carpathians, for instance, magnesites occur which have been formed into carboniferous limestones. They should show a greater porosity, but they are absolutely compact, dense rocks. All the points connected with the process of dolomitisation have not yet been cleared up, but dolomite can be formed in different ways. In many cases we have not only a simple replacement of one molecule of $CaCO_3$ but also very complicated interactions, and the formation of the double salt dolomite can take place even by adding material to $CaCO_3$.

The dolomitised Main Limestone was formed under lagoonal conditions and is often associated with gypsum, as can be proved in several sections.

Very complicated interaction takes place in the concentrated sea water of lagoons. It will not be the $MgCl_2$ which acts but the magnesium sulphate. Moreover, ammonium salts will play an important role. According to Murray and Irvine warm sea water contains much more ammonium salts than cold sea water, and we must expect warm sea water in lagoons where gypsum even is deposited. CO_2, derived from decaying organic material, will also be present.

It would be very interesting to study the question on lines similar to those of Van't Hoff's work on the different salts of the Permian salt deposits.

Dolomites connected with gypsum and salt beds display a characteristically cavernous structure. There is a framework of more or less dolomitised limestone, and between this framework are cavities, the walls of which are covered with dolomite crystals.

The framework does not fix the true porosity, and, as the late Mr. Whealler has shown, in accordance with the action previously mentioned, this framework would frequently have a porosity of only 1–7 per cent., and only half of this in the case of aragonite.

A good cavernous reservoir rock—such as the German " Rauchwacke "—is the result of the leaching out by solution, which takes place in lagoons, of certain parts of the limestone.

The transformation of parts of the limestone into dolomitic limestone, or sometimes into pure dolomite, is only one part of the processes resulting in a cavernous rock.

Mr. E. H. Cunningham-Craig said he desired, in the first place, to take the opportunity of congratulating the author upon his very comprehensive and well-balanced paper. He had shown a masterly grasp of the matter. He could confirm almost everything the author had said. Personally he remembered very well that when he first mapped the Maidan-i-Naftun field it was quite obvious that the minor structures that were seen at the surface would not continue to any great depth. It became perfectly obvious that a solid hard mass was lying underneath on the north-eastern side of the field, and probably at a very much greater depth on the south-western flank. He made up his mind that that hard mass could be nothing but the Asmari Limestone, but he did not realise that the Asmari Limestone would be the reservoir oil rock, that it would have been honeycombed by secondary changes, and so made into one of the most prolific oil rocks that was known. He was more concerned at that time with the detrital limestones, which were also affected very seriously and were made very strongly cavernous. He thought perhaps the author had not attached quite sufficient importance to those detrital limestones, which occurred very sporadically. In some places they were found very thick, and they then thinned out rapidly in each direction, passing into calcareous muds or even calcareous sands, thinning and finally disappearing. The existence of that limestone meant that some limestones in the immediate vicinity—he said " immediate vicinity " because they were so locally developed—were being denuded at the time the Fars Series was being formed. If a limestone was being denuded it was most likely that the limestone was the Asmari Limestone. Therefore, in the places in which the limestones were found very thick and very locally developed one might expect to find the surface of the Asmari limestone underneath considerably affected by denudation ;

and quite possibly that denudation had enabled the solutions which had caused those complicated secondary actions to attack that limestone the more rapidly. In that connection he desired to mention a curious point which the author had not mentioned. Some six or seven years ago he was sent four specimens of limestone, one of Asmari limestone and three which were labelled as the "main oil rock" from three different wells in the field. The Asmari limestone was fairly typical, showing the fossil forms which had been shown on the slides that evening. Another specimen was a highly crystalline and very cavernous dolomite, which consisted mostly of crystals of dolomite. The other two specimens were fine detrital limestones. Whether they occurred just on top of the Asmari limestone or not he did not know; he did not know from what depth they came in the well, but they were sent to him as the "main oil rock" from those three different wells. He thought it quite possible, therefore, that, in certain localities at any rate, on the top of the denuded mass of Asmari limestone, considerable deposits of detrital limestone might occur also, which, of course, would be dolomitised as well as the underlying Asmari masses. The author had very wisely stated with regard to the question of the origin of the oil that it could not yet be determined. Various theories existed as regard its origin, one which had not been mentioned being that oil was also indigenous to the Fars Series. That, he believed, was a point which Prof. de Böckh had not overlooked. Oil was to be found in a great many different horizons in Persia, and he believed they would certainly find oil indigenous to the upper Fars in other parts of Persia. He looked at the question in the following way. Although oil might have been formed in Cretaceous rocks it might have migrated, because it could migrate with the greatest ease if it were given sufficient time. Oil could migrate through limestone without leaving the slightest trace. It was only when colloidal beds were met with that the oil or part of it was seized upon; and that part which went through became filtered and therefore gave evidence of its migration. Given sufficient time, oil would migrate to enormous distances through rocks like limestone, and even shales and sandstone and anything that was not markedly colloidal. Every oil-shale field in the world gave evidence of that kind. The fact that oil was found in the Asmari limestone he looked upon simply as showing that the limestone when it was affected by secondary action was the best reservoir; that oil wherever it came from would always find the best reservoir and would stay there until it was washed out by water, or extracted by man, or removed in some other way. Although he did not wish to dogmatise upon the origin of the oil at Maidan-i-Naftun, he considered that it was the reservoir that must be looked for first, and when there was a

reservoir in the Asmari limestone it was known that it made an exceedingly prolific oil rock.

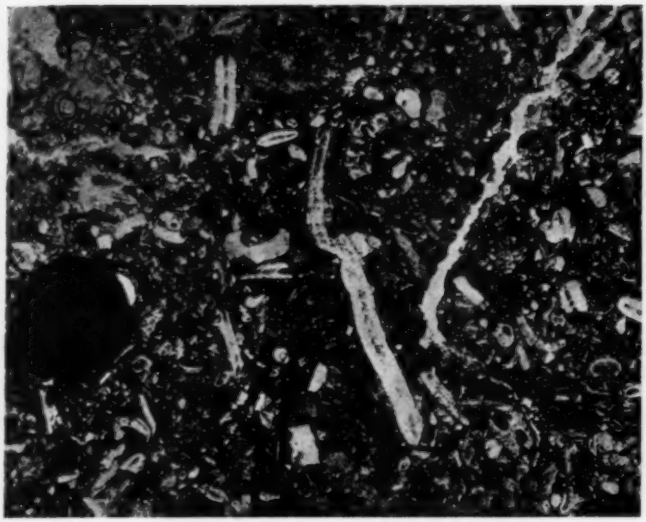
Mr. S. Lister James desired to identify himself with the very appreciatory remarks Mr. Cunningham Craig had made in regard to the paper. He thought it could be stated that the author himself deserved the credit for making the most important discovery of the identity of the main reservoir rock, the Asmari limestone. As had already been stated, it was previously thought that the main reservoir rock was one of the detrital limestones similar to those exposed at the surface, and in the early days there was no occasion to look further for the main source. Only the results of a very few wells were available for drawing a conclusion, and the slight irregularity of depth was then easily and plausibly explained by lenticularity—lenticular bands of the detrital limestone. But, as drilling continued, the difficulties of accepting that theory were accentuated. According to the Company's records, it was Prof. S. J. Shand who first suspected that the Asmari limestone was the real reservoir rock; but Prof. Shand only being in the Company's service a short time it remained for the author to develop that theory. Probably, for all he knew, the author might have formed that theory quite independently, but at any rate he carried it to finality, which was the main thing, by carefully examining a very numerous collection of slides made by himself or under his personal direction, and clearly demonstrating that there was no other course than to accept the Asmari limestone as the main reservoir rock. His important conclusions were confirmed palæontologically by Dr. J. A. Douglas. That discovery had marked a very great step in petroleum geology in Persia, and it had thrown an entirely new light on prospecting work in all parts of the country. It was necessary, in view of those results, to review their ideas of outside test areas with that fresh knowledge as a basis; that was the main fact that had to be depended upon. Prof. de Böckh had now brought them a great step forward in pointing out the association between the oil in the Asmari limestone and the development of a lagoon facies; and those were the two main facts upon which they now based their search for other fields.

Mr. T. G. Madgwick said that although he had no personal knowledge of Persia he desired to ask a few questions. In discussing the origin of the oil the author had referred to oil indications and oil shows. He would like to know which of those terms referred to seepages, and whether the author included bituminous matter in rocks as an oil indication. In describing the geological succession the author had frequently referred to a brown colorisation. Was that colour due to bituminous matter of any kind

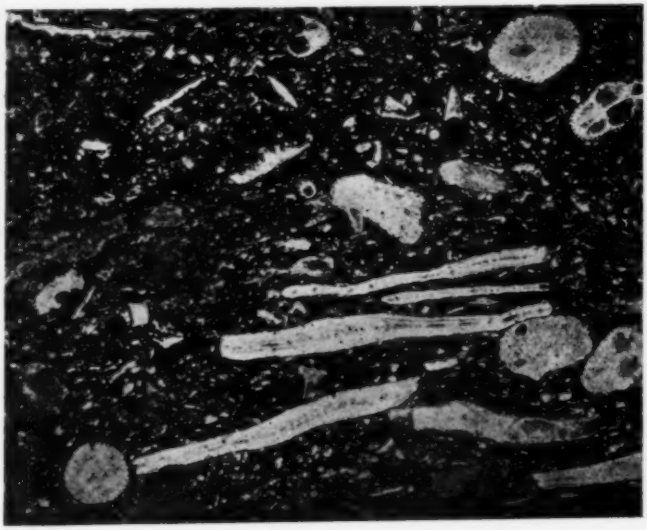
whatever. Further, the Asmari limestone was referred to as a highly organic rock. Was that because it contained tests of foraminifera, or because it had actual bitumen or any carbonaceous matter in it. He was very much interested in the suggestion that had been made that the Tang lines were lines of possible migration from depth. It would be interesting to know if those lines showed up in any way in the distribution of the oil underground or in the gas pressure, or whether they had any influence at all on the dolomitisation underground. The question of dolomitisation was a very important one upon which the author had thrown much light. The author evidently associated the occurrence of oil with dolomite, but he would like to know whether the author regarded the two as one phenomenon. It was not easy for him to imagine how the lagoon water could circulate through a massive limestone apparently to some depth, particularly if that limestone had not been fissured, and where there was a continually growing accumulation of more or less impervious sediments on top. That was a case in which core drilling would throw light on the actual occurrence, and perhaps the author had carried out experiments in that respect already. Some very interesting slides had been shown bearing on the significant fact recorded of the gypseous alteration of limestone. He noticed that the particular case described occurred in a faulted area and the author claimed that the alteration took place from below. That was certainly an occurrence which deserved the fullest investigation possible, and he would like to know whether the author considered it as something connected with the general process of dolomitisation. He also asked if there was any possibility of it having occurred on a larger scale prior to the deposition of the Fars group, and whether the resulting gypseous limestone, which would naturally be easily eroded, had played any part in the source of the gypsum in the Fars series. *Apropos* of that, he thought he might mention an occurrence in Sinai in which there was a Miocene limestone containing a very high percentage of gypsum, the partial erosion of which might very conceivably havf contributed a good deal to the gypsum deposits in that part oe Egypt. Did the author think any similar process had occurred in Persia ? He did not say that the Sinai occurrence was necessarily an alteration from below, as he had not considered it from that point of view. He also asked whether there were any seeps in the places where the gypsum occurred, and whether the occurrence of aragonite referred to was at all pronounced in the same locality. It was perhaps rather an unfair question to ask the author whether he were in doubt on the question of the organic hypothesis of oil, but would he raise the curtain further on the interesting discussions he had evidently been involved in with regard to the limestone, gypsum and hot water hypothesis.

Mr. Gordon Pitt said he did not know whether it was fortunate or unfortunate that whenever a geological paper or a paper with a geological trend was read before the Institution sooner or later the discussion seemed to direct its attention to the vitally important question of the origin of oil. He took it that the author's general observations in the paper, particularly in regard to the extraordinarily amazing list of identified animal remains which were mentioned, might be read in the light of supporting the animal origin of oil. One point had occurred to his mind several times, particularly during the remarks of their distinguished guest, Prof. de Böckh. The theories as to the animal, vegetable or purely inorganic origin of oil were usually definitely geological theories on the part of a geologist or definite chemical theories on the part of a chemist. The paper indicated most clearly that a man who was capable of bringing forward a reasonably tenable theory on either of those subjects must be immersed in his own particular branch of the subject. Therefore the problem very often was looked at from a prejudiced or biased point of view. The suggestion that had been made in regard to the ammoniacal condition of a solution when dolomitic changes were taking place furnished some information that might be overlooked. In forming a conclusion in regard to the animal theory on the one side and the vegetable theory on the other, an indication of that kind might be most valuable, because, apart from anything else, during the natural process of the production of oil from either an animal or a vegetable source certain chemical changes or chemical conditions were set up which were purely temporary, which left no final trace at all, and which would be likely to be overlooked by the geologist and might be overlooked or wrongly translated by the chemist. If it were remembered that animal material in undergoing the chemical changes which it must undergo in order to produce oil would unquestionably produce more ammonia than would be produced by a vegetable material, under corresponding conditions it might throw a certain amount of light on the subject, although the final evidence of that ammoniacal condition having obtained had entirely disappeared.

Mr. T. Dewhurst said that it must be admitted that great progress had been made since Messrs. Mayo and Busk read a paper to the Institution on the geology of Persia in 1918, owing to the excellent reconnaissance and detailed mapping of all members of the staff, and to the palæontological work of Dr. Douglas. The evolution of knowledge concerning the geology of Persia had recently been accelerated by the stratigraphical work of Prof. de Böckh. The members of the Geological Staff of the Anglo-Persian

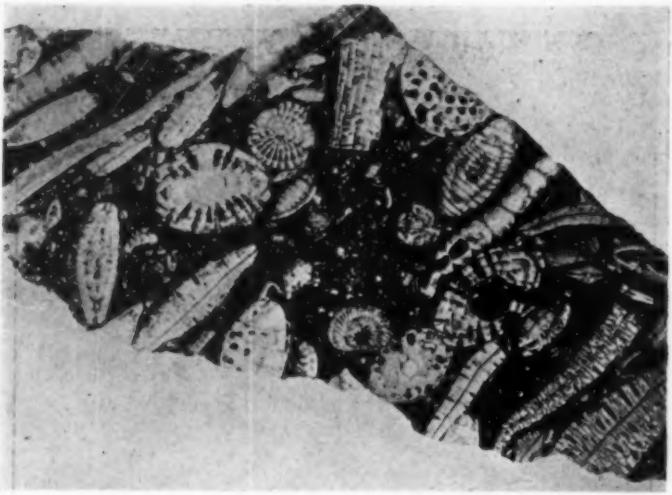


PHOTOMICROGRAPH OF ASMARI LIMESTONE (UPPER MIDDLE BEDS). BARD-I-QAMCHEH. DISPLAYING ALVEOLINA CF. MELO, MILIOLINE FORMS, LITHOTHAMNIUM AND HETEROSTEGINA.



PHOTOMICROGRAPH OF ASMARI LIMESTONE (MIDDLE BEDS). BARD-I-QAMCHEH. DISPLAYING HETEROSTEGINA AND ASMARIA.

PHOTOMICROGRAPH OF ASMARI LIMESTONE ; BASAL BEDS. BARD-I-QAMCHEH. DISPLAYING AXIAL AND EQUATORIAL SECTIONS OF LEPIDOCYCLINA.



PHOTOMICROGRAPH OF ROCKS FROM NUMMULITIC PHASE ; BASAL BEDS UPPER THIN-BEDDED LIMESTONE. DASHT-I-GUL. DISPLAYING ASSILINA, ORTHOPHRAGIMA AND NUM. GALLENSIS.

Oil Company had, in particular, hammered their way into the older geological formations of Persia, and had also raised some of the formations in the stratigraphical scale. For example, the Asmari formation had been shown to be mainly of Miocene age, while in the original paper it was considered to be older. Another important step in the progress of knowledge had been the recognition of the Asmari limestone as the main oil container, while further light had been thrown on the question of the Asmari-Fars unconformability. He agreed with the remarks of Mr. Cunningham-Craig in the latter connection. The recognition of the true age of the Asmari limestone had rather caused geological opinion to swing to the opposite extreme, and instead of postulating a big gap between the Asmari and Fars formations, to dispense with that gap altogether. The tendency now was to ascribe all the observed effects (such as those shown in the case of Maidan-i-Naftun, where there was striking discordance between the superficial Fars structures and the underground structure of the Asmari) to overlap, differential yielding to earth movement, and to the slipping and sliding of Fars beds down the slopes of Asmari cores. However, the detrital limestones of the Lower Fars suggested probable exposure and erosion of the Asmari limestone. Further, at Khamir, the Lower Fars, or beds with a Lower Fars facies, rested with some evidence of discordance on lower members of the Asmari limestone. Furthermore, in one section there was even a conglomerate at the base of the Lower Fars, indicating at least local unconformability. The lack of evidence of discordance in some sections might be deceptive. For example, in the Salt Range of India the Nummulitic Hill limestone was overlain by the Kamlials, and it was possible to examine the junction between these formations for miles without seeing any physical evidence of discordance. However, it was clear from palæontological and other evidence that the Charat series and the whole of the thick Murree series were missing, and that there was a big gap in the succession. Although palæontological evidence would not allow of a big stratigraphical gap between the Asmari and Fars formations, the apparent physical conformity in some sections might be deceptive. He therefore suggested that the observed effects between the Asmari limestone and the Fars should be ascribed to a plurality of causes—unconformability, overlap, differential yielding to earth movement, and the slipping and sagging of the soft Fars beds around Asmari cores. There seemed to be a lack of harmony between the various conclusions of the paper; there was no definite underlying thesis or conception or hypothesis. For example, the suggested conformability of the Asmari and the Fars was not correlated with the table showing the history of the earth movement to which the region had been subjected. Again, the postulate that the oil is indigenous to the

Asmari was not supported by the evidence as to the chemical and physical conditions under which the limestone was deposited. This lack of cohesion between the various conclusions and suggestions put forward constituted the main criticism of the paper. It was perhaps unnecessary to enlarge on the point made by Mr. Cunningham-Craig, with which he agreed, that the Asmari limestone may be the oil-container merely because it is a porous reservoir rock. Apart from the fact that there were many organic remains in the limestone, there was no more reason, from the evidence given in the paper, to believe that the oil was of Asmari origin than there would be to assume in the case of a sandstone field that the oil was formed in the oilsands. From the evidence of the paper, the porous Asmari limestone seemed to have no more claim to be considered as a source rock than had an oil-sand. There was no attempt to show that the conditions under which the limestone was deposited were favourable for the formation of oil. For several years he had suspected that the oil was formed in the Lower Fars inland seas and lagoons, and had migrated *via* the plane of unconformability and overlap into the porous portions of the Asmari limestone. This view was based largely on the existence of inland seas in Lower Fars times, on the fact that the most prolific seepages in Persia occurred in the Lower Fars detrital limestones and near the Asmari-Fars boundary, and on analogy with the Punjab oil occurrences. The Nummulitic Hill limestone of the Punjab resembled the Asmari limestone. There was unconformability and overlap of the Lower Charat beds, which were analagous to the Lower Fars, and like them were deposited under inland sea conditions. The analogy between the geology of the two regions was therefore striking. Geologists were agreed that in the case of the Punjab the oil was formed in the Lower Charat beds, and had migrated *via* the plane of unconformability and overlap into adjacent formations. The above-mentioned view of the origin and migration of oil in Persia was much strengthened by the completeness of the analogy with the Punjab. It would be very difficult, if not impossible, to eliminate that hypothesis. In any case, the postulate of indigenous Asmari oil required for its acceptance much more evidence than had been presented in the paper. It would seem to involve earth movement during the Asmari period, with the formation of an inland sea or lagoonal facies of the Asmari limestone. It was readily conceivable that under such conditions oil would have been formed in the Asmari limestone as well as in the Lower Fars beds, but the paper did not contain evidence in favour of the existence of such conditions. It was still more improbable, on the evidence submitted, that the whole of the oil in the Asmari limestone was indigenous to that

formation, and much more evidence should have been given before that hypothesis was formulated.

Mr. R. K. Richardson, in reply, said that Mr. Cunningham-Craig had referred to the particular samples of oil rock that were sent to him. Personally, although he had prepared some hundreds of slides, he had not seen anything in the nature of a detrital limestone from the main oil horizon. The particular specimen that Mr. Cunningham-Craig referred to, which was practically a pure dolomite displaying some crystalline matter, came from the central Maidan. Slides made from rocks in the central Maidan did not display many remains; they were practically all altered.

Mr. Cunningham-Craig said he desired to emphasise that two of the samples were not from the central Maidan area but from the south-eastern area.

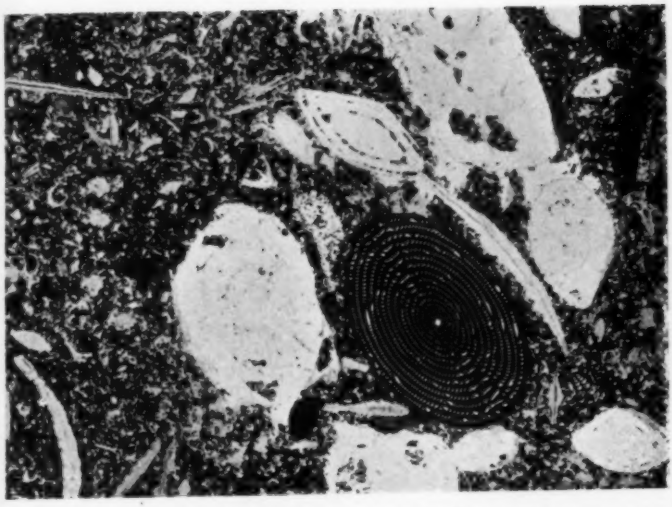
Mr. Richardson, continuing, said he could not think what they could be. He had made slides from the oil-bearing limestone out of every well, and they practically all showed those particular remains and a non-detrital character.

Mr. Cunningham-Craig said that all he knew was that they were the specimens sent to him.

Mr. Richardson, in reply to Mr. James, said he desired to emphasise that credit of priority for the suggestion that the Asmari limestone was the productive oil rock was due to Prof. Shand. The evidence submitted, in some respects, however, militated against the theory, which was subjected to criticism. He had carried on Prof. Shand's early work and brought it to a conclusion, removing at the same time the difficulties which stood in the way of its initial acceptance.

In answer to Mr. Madgwick, he said that the brown colour of the rocks mentioned in the paper was not due to organic matter; it was simply the natural colour. When he referred to the Asmari limestone as being highly organic he was referring particularly to the actual remains. With regard to possible tang lines, the evidence on the oilfield in regard to oil production, gas pressures and dolomitisation of the oil rock bore no relation to linear direction. He had put forward in the paper two alternative views with regard to the occurrence of gypsum in pre-Fars formations. There was distinct evidence in Persia of widespread secondary action, not merely in the Asmari limestone but in the Fars limestones and in the Hippuritic limestone of the South. Gypsitisation had taken place along joints in the Hippuritic limestone and in some cases in Fars rocks as at Marmatain; for example, whole beds 10–30 ft.

thick had been almost entirely changed to gypsum. If they were given a blow with a hammer they crumbled into a dust of fine gypsum and fragmentary limestone; they were full of cavities and consisted largely of gypsum, which was obviously secondary after limestone. The source of the gypsum in the Fars was not secondary at all; it had been laid down as a primary deposit in the desiccated seas of Fars times. The association of aragonite with oil seepages was an extraordinary occurrence in Persia. It had been noted by geologists in the south and in the north; it occurred in the Maidan-i-Naftun oilfield, and it was certainly a very intriguing occurrence. He understood that what Mr. Pitt desired to know in the remarks he had made was whether he was in favour of the animal origin of oil. As a matter of fact, on the basis of evidence at present available, he was distinctly in favour of an indigenous animal origin for the oil in the Asmari limestone; but it was necessary to put the other views forward because, as he had stated in the paper, it was absolutely essential to preserve an open mind. Objections could be brought against all hypotheses particularly upon such a debatable subject, but he considered an hypothesis involving an indigenous origin in the Asmari limestone fraught with the least difficulties. Conclusive evidence did not exist, and it was necessary to keep an open mind about the whole question. He was in entire agreement with the remarks Mr. Dewhurst had made with regard to the plurality of causes accounting for conditions at Maidan-i-Naftun. He considered the actual discordance was due to a number of causes which he had already indicated in the paper. Although he had pointed out the conformable nature of the Fars Asmari junction over hundreds of miles of mapped outcrop he had already stated that a condition of conformity with overlap represented the actual initial nature of the junction. With regard to the physical relations of the two groups in reference to earth movement, the cohesion between the two was distinctly shown in the table in regard to tectonics. Formation of fold lines at the end of Asmari times, and gradual uplift during Fars times, with attendant overlap of deposits against the flanks of rising Asmari masses, were indicated in the table referred to. Mr. Dewhurst had commented that, apart from the fact that there were many organic remains in the limestone, there was no more reason to believe that the oil was of Asmari origin than there would be to assume in the case of a sandstone field that the oil was formed in the oilsands. He considered, however, that the origin of the oil could not be contemplated apart from the abundant organic remains. Their presence was an integral part of the hypothesis. He had put forward in the paper an hypothesis in regard to the origin of the oil. Mr. Dewhurst was in possession of as much information as he was on that subject.



PHOTOMICROGRAPH OF ROCK FROM NUMMULITIC PHASE; BASAL BEDS UPPER THIN-BEDDED LIMESTONE. DASHT-I-GUL. DISPLAYING ALVEOLINA OBLONGA, ORBITOLITES, ORTHOPHRAGIMA AND NUM. URONIENSIS.

The President thought the Institution was to be congratulated on the fact that at the last meeting of the Session such an exceedingly interesting paper had been read. All the speakers who had taken part in the discussion had referred to its excellence. He had much pleasure in asking the members to pass a most hearty vote of thanks to the author of it.

The resolution was carried with acclamation and the meeting terminated.

Mr. W. G. Weeks subsequently wrote :—I agree entirely with Mr. Dewhurst's remarks that insufficient evidence has been adduced to justify our regarding the Asmari limestone as the origin of the oil it contains. Mr. Richardson's description of the limestone—" a highly organic rock composed almost entirely of foraminiferal remains "—would apply very well to the chalk, in the whole enormous mass of which, so far as I am aware, no trace of oil has been found ; so that the mere presence of multitudes of tests proves nothing.

I should like to ask Mr. Richardson whether he has ever considered the spatangid shales as the possible mother-rock of the oil. The occurrence of this 250 ft. of shales, lying conformably between limestones, suggests the approach and retreat of a coast-line, some river-mouth in which supplied the material for the shales. Since, during the Palæogene, the Mediterranean Sea was much larger than it is now, extending far to the east of the Caspian, there was sea to the north-west, north, and north-east of the Persian area, and the river, whose mouth discharged the spatangid shale material, presumably came from the south-west, south, or south-east.

Palæogeographical researches indicate that, in the Cretaceous and Palæogene, a great trough lay to the east of the African land-mass, its axis running from a point north of Madagascar across the Arabian Sea and Baluchistan to the then eastern extension of the Mediterranean. The trough appears usually to have been submerged by a southward-trending arm of the ancient Mediterranean ; but, at some time early in the Eocene, it is thought to have been above sea-level for a while. During the period of emergence it would have been drained by a northward-flowing river which might very well have been the one which supplied the material for the shales.

This river, both in its attitude to the climatic zones and in size, would have been closely comparable with the Nile. Now it has been estimated that the Nile brings down annually, in solution alone, about 1,700,000 tons of organic matter. It is probably no exaggeration, therefore, to say that our hypothetical river might have delivered into the sea, along with its load of inorganic material, a quantity of the order of 5,000,000 tons a year of dissolved and

finely comminuted suspended organic matter. The inorganic material, certainly, would have been deposited round about the delta; and it is not unreasonable to suppose that it would have carried down with it at least some of the organic. I suggest that this precipitated organic matter was the primary material of the Asmari oil.

The hypothesis obviously needs a good deal of confirmation by field observation and otherwise. I believe, however, that it does not contradict any known observation, and it has the merit of reconciling the views of those who advocate an Asmari origin because of the difficulty they find in understanding how, otherwise, the oil got there, and of those who cannot accept that theory.

STUDENTS' SECTION, LONDON BRANCH.

THE THIRD GENERAL MEETING OF THE STUDENTS' SECTION, London Branch, was held at Aldine House, Bedford Street, Strand, W.C. 2, on Tuesday, December 18th, 1923, at 6 p.m.

Mr. H. G. Austin (Chairman), in opening the meeting, stated that, owing to Messrs. C. O. Graham and F. E. J. Foxall-Smedley's absence abroad, which necessitated their resignation on the Committee, it was decided to fill their places, and Mr. L. W. Marrison had been selected to fill one vacancy, the other being left open until later.

Mr. A. B. Miskin was then called upon to read his paper, an abstract of which follows, entitled :—

The Iodine Values of Cracked Gasolines,

by A. B. MISKIN.

This paper embodies the results of some research on the iodine values and other properties of the olefines in cracked, untreated, motor spirit.

Dr. Dunstan very kindly supplied the three samples which were examined—Ramage vapour phase cracked spirit, Ramage spirit once distilled over dried, unburnt clay, and soda treated, and A.D.H. cracked gas oil.

Before proceeding further it will be necessary to outline the chemistry of these oils, for the benefit of those students who are not chemists.

Five hydrocarbon types are found in these oils—namely, Paraffins, *e.g.*, methane CH_4. These do not react with ordinary reagents at room-temperature, or with halogens in the dark. Next in order of stability are the aromatics, *e.g.*, benzene C_6H_6, which resemble the paraffins in their behaviour, except in that they dissolve in 98 per cent. sulphuric acid. Thirdly, there the olefines, *e.g.*, ethylene C_2H_4. These compounds are characterised by one "Double bond" and hence are less stable than paraffins. They combine with 80 per cent. sulphuric acid and with halogens even in the dark. Fourthly, there the diolefines, which are similar to the olefines, but have two double bonds, are less stable and will dissolve in weaker acid. Finally, acetylenes are found in cracked oils. Acetylenes have a treble bond, are very unstable and will combine with sodium to form acetylides. It is possible that diolefines also react in this manner.

It must be remembered that in the above examples only the simplest compounds are quoted, not those which generally occur. It was desired to find the iodine value of the olefines alone, so an attempt to remove the diolefines and acetylenes was made. This was done by treating each oil with sodium dust, which was prepared by boiling sodium in toluol. On treatment there was discoloration of the oil accompanied by a slight diminution of volume (see Table A). However, it is doubtful whether all the diolefines were removed. They are only present in small quantities.

Iodine Value.—The iodine value of an oil may be defined as the weight of iodine, or other halogen, expressed as iodine, which combines additively with 100 grms. of the oil. In these experiments Wijs' solution of iodine monochloride in glacial acetic acid was used. The method was to weigh out 0·05—0·3 grm. of oil in a small glass bulb which was crushed under carbon tetrachloride in a reagent bottle. To this was added 25 c.cs. of reagent by a pipette. The bottle was then left in the dark for a given time. To prevent the escape of halogen from the bottle the stopper was dipped in a 10 per cent. solution of potassium iodide, thus forming an "Iodine seal." After the reaction the residual iodine monochloride was decomposed with potassium iodide. Thus the residual halogen was replaced by an equivalent amount of iodine, which was estimated by titration with decinormal sodium thiosulphate, using a starch indicator.

Since the amount of reagent used influences the amount absorbed, the excess of halogen is here expressed as the ratio :—

$$\frac{\text{Iodine not reacted on}}{\text{Iodine absorbed by oil}} = k$$

Before determining the iodine value for the Ramage spirit it was once distilled to remove the excessive gum. The iodine values for different "Excess-concentrations" are shown in Table A and Fig. 1. The curves show that time and excess of reagent have a very marked effect on the iodine value, and that the relation between them is regular, but not linear. The absorption of iodine seems to be complete for a reaction of twelve hours with an excess concentration of about ten. The value has been taken as 128(0·3).

The values for the A.D.H. cracked gas oil (Table C and Fig. 2) indicate that the time of reaction is here relatively more important than a high excess of reagent; also that the iodine value seems to go on increasing indefinitely. The final value has been taken as 125. It may be higher.

No estimations were made for the treated Ramage spirit. However, two values were found for the untreated oil at different temperatures with a high concentration and a reaction period of twenty-four hours; these results are given in Table D. From

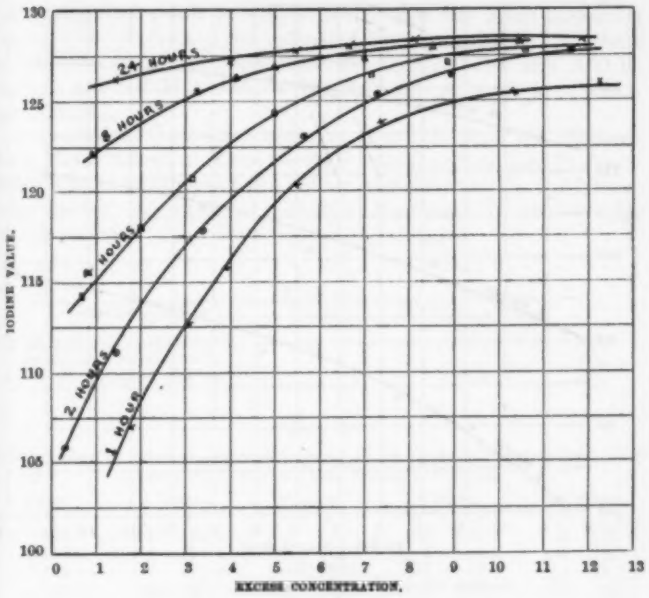


FIG. 1.

IODINE VALUES, RAMAGE SPIRIT.

these figures it would appear that temperature influences the degree of absorption of iodine. Probably the value for 50° C. is so high because substitution is taking place to some extent.

These general conclusions are borne out by the work of Farragher Gruse and Garner (*J. Amer. Soc. Chem. Ind.*, 1921).

Sulphuric Acid Values.—The sulphuric acid value (S.A.V.) may be defined as the percentage of oil absorbed on treatment with strong sulphuric acid.

It is said (*J. Inst. P. T.*, 1918) that 80 per cent. acid will absorb the olefines, diolefines and acetylenes, but not the paraffins or aromatics; Brookes and Humphries (*J. Amer. Chem. Soc.*, 1918) say that this statement is only approximately correct. Nevertheless, it has here been assumed that, if the diolefines and acetylenes have been removed from the oil, the sulphuric acid value is a measure of the olefine content. This value was found by shaking the oil and acid together in a separating funnel in a stream of cold water; the acid is allowed to settle down for twenty-four hours. The new volume of oil is then read off. Treatment is repeated with

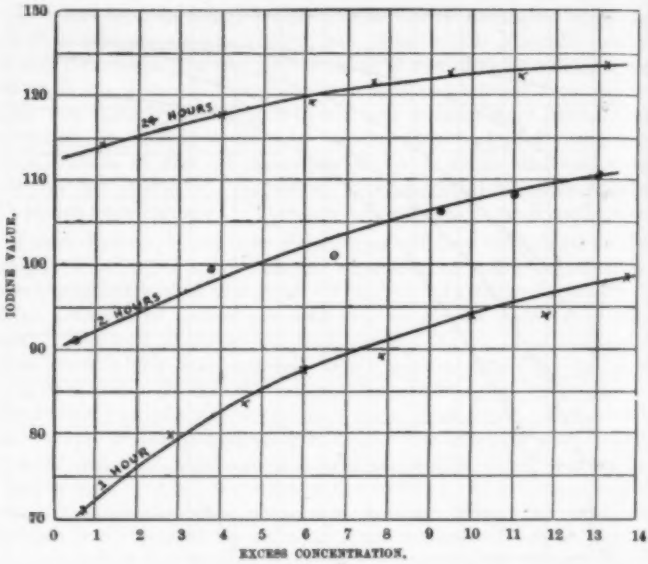


FIG. 2.

IODINE VALUES, A.D.H. CRACKED GAS OIL.

fresh acid until there is no further contraction of the oil. Considerable heat is liberated in the reaction and various gases are evolved, chiefly sulphur dioxide. The Ramage spirits gave contractions of 64 per cent. and 69 per cent., respectively, for the treated and untreated oils, both becoming dark and opaque on treatment. This opacity seemed to be due to a dark brown precipitate. The acid oils formed very bad emulsions with water, which would not break down. The value for the A.D.H. cracked gas oil was 56 per cent., and the oil remained transparent throughout although it darkened.

Mean Molecular Weight of the Olefines.

Let the iodine value be V
" " sulphuric acid value be .. .. $x\%$
" " mean molecular weight of the olefines be .. .. M
Then in 100 grams oil there x grams olefines.
Hence V grams iodine combine with x grams olefines.
But 2 atoms of iodine combine with 1 molecule of olefine.
254 grams " " " " M grams " "

$$\frac{254}{V} = \frac{M}{x}$$

$$\text{or, } M = \frac{254.x}{V}$$

Applying this result it will be found that the mean molecular weight of the olefines in the untreated Ramage spirit is 127, which corresponds to an average molecule C_9H_{18}. For the A.D.H. cracked gas oil M is 114, or the average molecule is approximately C_8H_{16}.

In conclusion, the author desires to thank the Staff and Students of the Royal School of Mines for their assistance, and also Professor Watts who so kindly gave the author permission to use the laboratories during the vacation. Finally, he wishes to acknowledge his indebtedness to Dr. Dunstan, for the samples.

TABLE A.

Contractions of Oils on Treatment with Sodium Dust.

Ramage untreated spirit	6%
Ramage treated spirit	4%
A.D.H. cracked gas oil	4%

TABLE B.

Iodine Values of Ramage Untreated Spirit, at 18 C, for various Values for k (Excess-concentration) and Reaction Periods.

1 hour.		2 hours.		4 hours.		8 hours.		24 hours.	
k.	I.V.	k.	I.V.	k.	I.V.	k.	I.V.	k.	I.V.
1·8	107·1	0·3	106·0	0·7	114·1	0·9	122·1	1·5	126·1
3·1	112·6	1·4	111·4	2·0	118·1	3·3	125·8	4·0	127·0
3·9	116·0	3·4	117·9	3·1	121·2	4·1	126·4	5·5	127·2
5·5	120·5	5·6	123·3	5·0	124·6	5·0	126·9	6·6	128·0
7·4	124·0	7·2	125·6	7·2	126·7	7·0	127·2	8·1	128·3
10·4	125·4	8·9	127·0	8·5	127·0	8·5	128·0	11·9	128·3
12·1	126·2	10·6	127·5	10·6	127·8	10·4	128·3		—
	—	11·6	127·9	11·6	128·0		—		—

TABLE C.

Iodine Values of A.D.H. Cracked Gas Oil.

1 hour.		2 hours.		24 hours.	
k.	I.V.	k.	I.V.	k.	I.V.
0·6	71·5	0·5	92·0	1·2	113·8
2·9	79·8	3·9	99·8	4·0	117·6
4·6	83·6	6·6	100·3	6·1	119·0
6·0	87·0	9·2	106·5	7·6	120·9
7·8	88·3	11·0	108·0	9·5	122·5
10·0	93·1	13·0	110·2	11·2	122·3
11·7	94·2		—	13·2	123·7
13·7	98·4		—		—

TABLE D.

Effect of Temperature on the Iodine Value of the Untreated Ramage Spirit, the results being reduced for Standard Conditions, when k 10, and t 24 hours.

Temp.	I.V.
0° C.	123·5
18	127·9
50	134·1

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DISCUSSION.

The Chairman thanked Mr. Miskin for reading a very interesting paper, especially to those interested in experimental work.

Mr. Garlick said that in order to obtain the results which the author had mentioned, some seventy to eighty separate determinations had been made, and he thought the results could be taken without question.

The whose subject of cracked gasoline is an important one. At the present time it is doubtful as to whether any oil company would be willing to admit that their motor spirit contained such a constituent. It is, however, becoming increasingly difficult to meet the demand for the more volatile fractions of petroleum, and

cracking will be resorted to more and more. At present the knowledge of the characteristics and behaviour of a cracked gasoline is extremely meagre. It is stated that it tends to form gummy deposits in the internal combustion engine, and to increase carbonisation troubles. Before long, however, cracked gasolines will be very much to the fore, and it is in opening up a method of examination and comparison that the value of this paper lies.

He would like to ask Mr. Miskin as to whether he could state a little more about the oils with which he was dealing ?

It would be useful to know the origin of the cracked oils and their boiling ranges and specific gravities. Were there present any aromatics in his oils ? If so, these would tend to influence his results at higher temperatures and longer times.

The American Society for Testing Materials have recommended a method for determining the iodine value of a fuel. Can Mr. Miskin state as to whether this method gives reliable and repeative results, even if only of an empirical character ?

At what temperature and under what conditions does he consider an iodine value determination should be carried out in order to obtain the maximum knowledge ?

Referring to the " sulphuric acid value " of an oil, does Mr. Miskin mean " total unsaturated " by this ? In a standard method shaking is continued for one hour—not less—when extracting with sulphuric acid. Also to avoid emulsions, which so readily form on attempting to wash an oil after sulphonation, shaking with a mixture of equal amounts of ground lime and calcium chloride is useful.

In conclusion, he expressed his thanks for the most interesting paper, and hoped that Mr. Miskin would return to this work at some later date.

Mr. L. W. Marrison said that if the acetylenes present in the gasolines were of high molecular weights, they would, in part at least, be of the completely alkylated type and so be unattacked by sodium dust ; in this case they would contribute to the iodine value.

He further stated that the " critical temperature " of the reaction of the olefines with acid seemed contrary to those facts of chemistry, which is that every chemical reaction occurs to some extent, even at low temperatures, and that this reactivity increases gradually with temperature.

The " muddiness " of the acid-treated oil might be due to the free carbon forming a colloidal solution, probably a gel, or a solid solution.

The effervescence noted when sodium was added to the oil might be due, it is suggested, to the acids present in the cracked gasoline.

Mr. A. Rauch asked whether potassium permanganate had been used for estimating unsaturated compounds, and whether it would not have been better to have rinsed the separating funnel out with acid, when determining the sulphuric acid value, instead of letting the funnels drain for a considerable period ? He agreed with Mr. Garlick in thinking that the weight of oil used in the estimation of the iodine value was too small.

Mr. Miskin, in reply to Mr. Garlick, said that he was now able to give the gravities of the oils, which Mr. Gwinner had kindly determined for him. The values were as follows :—

Ramage untreated spirit	..	..	0·8493
Ramage treated spirit ..	..	..	0·7954
A.D.H. cracked gas oil ..	..	..	0·7772

The original crude oils, he understands, all came from Persia and were of a napthenic type ; the aromatic content of the straight-run gasoline was 10 per cent., and appears to have been considerably less in the cracked gasoline.

With regard to the method suggested by the A.S.T.M., the results will probably vary by a unit or two when the iodine value exceeds about 30. For low iodine values, say up to 15, the results will be pretty constant. In general, the values will be comparable so long as the temperature and excess concentration are kept constant. In this method the experiment is so arranged that about one-third of the reagent is used. Under such conditions the test is reliable.

For full absorption by the unsaturated compounds, other than aromatics, the temperature should be below 20° C., and the amount of reagent absorbed should not exceed one-tenth of the amount used for a reaction of twenty-four hours.

The sulphuric acid value is, in this case, the olefine content. Aromatics will not be absorbed if the temperature is kept down. The other unsaturated bodies had previously been removed by the sodium dust treatment.

The author is not familiar with the use of lime as an agent for breaking down emulsions.

In reply to Mr. Marrison, the author considers that the acetylenes, if completely alkylated, would be saturated and so would not influence the iodine value. If, however, they were unsaturated, they would be attacked by the sodium.

The term, " critical temperature," was not meant to be absolute, but rather the temperature at which the reaction became important. It is possible that the reaction is analogous to that of the nitration of benzene; above 50° C. the yield of dinitrobenzene, as opposed to mononitrobenzene, becomes important.

It is quite possible that the "muddiness" of the acid-treated oil was due to colloidal carbon, but one cannot be definite until some work on the subject has been done.

The effervescence might be due to either acid or water. The latter is more likely to have been present, as in two cases the oils were not treated in any way after leaving the still.

With regard to Mr. Rauch's question on the use of permanganate for the estimation of the olefines, the method seems quite feasible. The dyed alcohols could be converted into amines, which could be estimated in a nitrometer.

Rinsing the funnel while draining would certainly cause a recommencement of the reaction: the oil would heat up and so absorb some of the aromatics. Such absorption had to be avoided in this experiment.

Finally, the same weight of oil has been used successfully by other investigators in similar experiments. Were much more to be taken, it would be necessary to work with much stronger standard solutions, such as normal iodine monochloride and perhaps semi-normal thiosulphate. Otherwise, the volume of liquid would become inconveniently large.

STUDENTS' SECTION, LONDON BRANCH.

THE FOURTH GENERAL MEETING OF THE LONDON BRANCH OF THE STUDENTS' SECTION was held on Tuesday evening, January 29th, 1924, at Aldine House, Bedford Street, the Chair being taken by Mr. H. G. Austin.

An abstract of the paper read follows:—

The History and Geology of the Oilfields of Mexico.

By C. A. SANSOM.

The Oil Industry of Mexico dates back to the year 1882, when the first well was drilled at Viego, West of Tuxpam. It was not, however, till 1901 that oil was obtained in commercial quantities (near Ebano), and in that year the output amounted to 10,000 barrels. The industry expanded rapidly during the next few years under the pioneering enterprise of Messrs. S. Pearsons and Sons, and in 1907 the production reached 1,000,000 barrels. In the next year the Dos Bocas field was discovered, and the output rose to 3,500,000 barrels.

In 1910 the Casiano and Potrero fields were brought in, the initial well, Casiano No. 7, giving 25,000 barrels a day, and the famous Potrero No. 4 over 100,000 barrels. Both of these gushers were eventually brought under control.

About the same time oil was proved in the Topila and Panuco areas, and the production rapidly mounted to over 25,000,000 barrels in 1913. In this year the big Alamo field, West of Tuxpam, was discovered.

In the following year and during 1915 considerable trouble was caused by political disturbances, and for a time drilling was completely stopped. Moreover, shipping facilities were curtailed in the years following on account of the war, and many of the largest gushers were partially shut in. However, the output continued to increase, and by 1916 it had reached 40,000,000 barrels.

GEOLOGY OF THE OILFIELD REGIONS.

The rocks covering the greater part of Eastern Mexico are cretaceous and tertiary. The important oil strata are the lower cretaceous Tamasopa limestone and the upper cretaceous San

Felipe limestones and shales. Oil is found also, when structural and physical conditions allow, in the cretaceous-eocene Mendez shales. It occurs in anticlines and domes, usually accumulating in fissures and cavities in the shales and limestones. The rocks are traversed by basaltic dykes, which not only dome the strata and thus produce a normal trap, but also render the rocks porous and cavernous, and themselves form important barriers to migrating oil.

Both the Tamasopa and San Felipe limestones are considered to be mother rocks. Movement of oil is rendered very easy and rapid owing to the extensive underground fissures, and the rock pressure is considerable. Conditions are therefore ideal for large gushers.

The general strike of the rocks of North-Eastern Mexico is approximately N.S. In the Isthmus of Tehuantepec and in Yucatan and Tabasco the Caribbean fold system is strongly felt, and the strike is E.W. The general dip in the north is easterly away from the mountains, and at the coast thick Pleistocene deposits obscure the solid geology.

Drilling Methods.

Heavy combination rigs are generally used, the rotary for traversing the newer soft formations, and the cable tool for penetrating the massive cretaceous limestones. Drilling costs are usually high, being accentuated owing to difficulties due to the great rock pressures. These have been as high as 1000 lb. to the square inch. Wells are usually under 2000 ft. in depth, though in the north 4000-ft. holes have been drilled.

Pipe-Lines.

These have been, up till recently, unable to cope with the enormous supplies of oil available. A 6-in. and 8-in. series of pipes connects the main oilfield regions with the ports of Tampico and Tuxpam, and the system has been greatly expanded during the last few years.

Type of Oil.

There are two main types—the Northern Heavy Oil (sp. gr., 0·973 to 0·993), and the Southern Light Oil (sp. gr., 0·922 to 0·947). In addition there is the oil found in the Isthmus of Tehuantepec (sp. gr., 0·792 to 0·881), which yields a fair percentage of benzine and a high grade lubricating oil. The Tampico oil is very viscous, and is often mixed with a lighter type in order to accelerate its flow through the pipes.

Development in 1916 and Later Years.

Early in 1916 the great Carro Azul No. 4 gusher was brought in at over 250,000 barrels daily, being one of the largest gushers ever known. This was followed in 1918 by the discovery of two large fields—the Naranjos and Tepetate. Both were noted for their enormous gushers, daily flows of 90,000 barrels a day being not uncommon. The year 1918 was also notable for the flooding of many of the older fields by salt water. One of the first wells to be affected was the famous Potrero No. 4, which yielded salt water very suddenly in December, and it was soon followed by other wells in the same field. This phenomenon was unique in its way, as many powerful producers changed to salt water in a single night.

The year 1918 also witnessed the end of the two big oilfields of Casiano and Tepetate, which in their brief existence produced an enormous quantity of oil. In 1919 the production rose to 87,000,000 barrels, representing more than 12 per cent. of the total output of the world for that year.

In 1920 as many as fifty-one new wells were drilled in different parts, of which thirty-three were productive. Most of these were situated in the small competitive area of Northern Amatlan and Southern Chinampa, and this overdrilling soon led to a rapid incursion of salt water into the deeper wells. The Southern Chinampa pool quickly declined and was soon followed by the Los Naranjos field.

These declines were partially offset by the discovery, in October 1920, of the Zacamixtle field, which grew rapidly in importance. A new area was also opened up south of Los Naranjos, and in the first nine months of 1921 sixty-three new wells were completed in and around this district.

Throughout 1921 salt water was steadily rising in the Amathan field, which had produced a large quantity of oil during 1920. By September 29th the edge water had reached the top of the structure, and the field became to all intents and purposes derelict. About the same time the Zacamixtle field also became a victim, and its large gushers turned one by one to salt water.

The elimination of these two fields so early was entirely unexpected in authoritative quarters. It had been hoped that the Amatlan-Zacamixtle pools would take the place of the exhausted Los Naranjos, and their failure to do so upset all calculations.

The year 1922 was chiefly remarkable for the rapid rise of the Cerro-Azul-Toteco pool, which at one time produced 400,000 barrels daily. A decline, however, set in, and by December the output had dropped to 175,000 barrels a day. In this year the

production of the Panuco fields increased rapidly, so that by the close they were giving 30 per cent. of the total for the country.

This rise was continued throughout 1923, and in March, for the first time since 1910, the Northern and Southern Fields produced an equal amount of oil. As the Panuco oil is a heavy one, the proportion of light oil to the total declined from 83 per cent. in 1921 to 43 per cent. in 1923.

Recent Operations.

These have been greatly restricted owing to revolutionary troubles, but have been practically confined since the latter part of last year (1923) to the Cacalilao (Northern) district, the Isthmus of Tehuantepec, and a small area north of the Alamo field. The only real success met with has been in the Cacalilao district, the total production from this area having been at the rate of over 100,000,000 barrels yearly. The Isthmus, where the occurrence of oil is somewhat similar to that in the Gulf cretaceous fields of the U.S.A., has been disappointing, but drilling is being continued. This area, together with the States of Tabasco, Yucatan and Quintana Roo, may be described as the most hopeful area at the present time. The Cacalilao field cannot now be far from its peak of production (if it has not already reached it) and, if political conditions allow, the areas mentioned should be worthy of exploitation. Time alone will show whether they will become even a good second to the old exhausted fields of Eastern Mexico.

The Chairman (Mr. H. G. Austin) said they had all listened to a most interesting paper. He did not think the paper lent itself very well to discussion, but hoped that some of the members present had some questions to ask.

Mr. A. B. Miskin asked whether the author could give him some idea of the fauna of the Tamasopa limestone. Was it exclusively marine; and were there, in the San Felipe series or in the beds above, any foraminiferal marls. He would also like to know whether the intrusion of basaltic rock often resulted in the drying up of the oil in the shatter belt round the intrusion. What was the probable source of the volcanic ash met with in the Isthmus of Tehuantepec, mentioned in the latter part of the paper? He would like to know whether caving took place in the rocks shattered by intrusions. Was there any definite evidence of the relation of oil accumulation to the ancient shore lines in the district, and where were these shore lines?

Mr. T. G. B. Davies asked what might be the probable cause of the oilfield fires occasionally experienced.

Mr. Sansom, in reply, stated that very little was known about the fauna of the Tamasopa limestone. He referred Mr. Miskin to Garfias's paper on "The Oilfield Region of N.E. Mexico (*Econ. Geol.*, Vol. X., pp. 195-224), and also to the numerous other references in the Bibliography which he could supply. The fauna of the Tamasopa was unquestionably marine. He regretted that he had no information regarding the occurrence of foraminiferal marls, but suggested that foraminifera were found in the Eocene Mendez shales.

He did not think that intrusion of igneous rocks resulted in the drying-up of the oil. His conception was that the intrusions took place prior to oil migration, which was arrested in the cavernous spaces thereby formed.

The direction of oil migration was westerly towards the main mountain masses, whose easterly edge probably coincided approximately with the ancient shore line.

With regard to the formation of the volcanic ash, this might have been produced either by a submarine eruption or by a big volcano in the Otontopec region to the north-west. He did not suppose that caving took place owing to intrusions, as the rocks were resistant and would be indurated by the heat of the rising volcanoes.

In reply to Mr. Davies, the main cause of oilfield fires was :—(1) The ignition of oil vapours coming into contact with the flames under the boilers. This was the case in the Amatlan fire. (2) Lightning striking a well, as in the case of Petrero No. 4. (3) Carelessness among the workers on the derrick.

The Constitution of Asphalt.

By F. J. Nellensteyn.
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There is scarcely any field in which organic chemistry has met with so little success as in that of the bitumens, particularly asphalt. A consideration of the views of the best-known workers in this field and the definitions given by them clearly demonstrates this statement.

Engler (Engler-Höfer, *Das Erdöl*, vol. 1, 1913, p. 671) lays stress upon polymerisation reactions, Marcusson (*Die natürlichen und künstlichen Asphalte*, 1921) considers the oxygen and sulphur compounds as essential constituents of asphalts, whereas Abraham ("Asphalt and Allied Substances," 1920, p. 23) considers these as by no means essential but rather as accidental.

In this discussion, therefore, we decided not to start with any definition of asphalt, this being practically impossible from the vague data at our disposal, but to aim at the production of a definition as a result of our researches. Although it is impossible to give a precise definition of asphalt, it is easy to determine whether a substance contains asphalt or not by making use of the following facts :—(1) All asphalts belong to a class of organic bodies which are easily distinguishable from all other classes. (2) In this class there are different groups, and the asphalt group has characteristic properties.

The class to which asphalt belongs is that of the bitumens—*i.e.*, substances containing carbon and hydrogen in large percentages, which on distillation at atmospheric pressure yield a distillate consisting essentially of hydrocarbons. From other bitumens asphalt can be distinguished by the following properties :—

Colour.—Asphalt is dark brown to black; the benzene solution, even when much diluted, is dark brown and never clear. Other bitumens are generally colourless or light yellow.

Behaviour on Congealing.—Asphalt when solidifying shows a very marked increase in viscosity without crystallisation. Other bitumens show either crystallisation or a gradual increase in viscosity.

Behaviour on Distillation.—Asphalt always remains as a residue. The distillate from an asphalt always displays characters very different from those of the residue, whereas in the case of other bitumens the difference is only one of degree.

Solubility.—Asphalt differs from most other bitumens in being partly insoluble in benzene of low boiling point.

Substances showing these asphalt characteristics have, however, no definite chemical composition, so that asphalt must be regarded as a mixture of different substances.

The first question which arises is, therefore, Is asphalt a mixture containing only asphaltic substances? The answer is, No, as distillation separates asphalt into a distillate and a residue. This might be attributed to decomposition were it not for the fact that a similar separation can be effected at O°C by treatment with benzine of low boiling point.

The asphaltic substances which constitute the essential part of asphalt are called *asphaltenes*, a name originally proposed by Boussingault (*Ann. Chim. Phys.*, 1837, II., 64, 141). The problem thus resolves itself into a study of these asphaltenes. At once a great difficulty presents itself—viz., that of the purification of these indifferent substances. This bars the way to a direct attack on the problem, which must therefore be approached by the study of the formation of these bodies by the distillation or oxidation of hydrocarbons.

Distillation of Hydrocarbons.

Asphalt is formed by the distillation of almost all of the higher hydrocarbons. We have now the choice of investigating this asphalt formation from a great number of hydrocarbon mixtures and drawing general conclusions therefrom, or of choosing a particular mixture of hydrocarbons which seems to display the reactions in their simplest forms. We chose the last way.

A suitable substance was found in a mixture of hydrocarbons, a distillate from a Borneo asphalt base oil. This distillate had the following properties:—

Sp. gr. at 15° C.	0·9555
Carbon	87·0%
Hydrogen	11·0%
Sulphur	traces
Nitrogen	nil
Oxygen	2·0%

This is a typical asphalt-base oil distillate (high sp. gr., low H percentage, traces only of S & N).

Distillation of this oil with superheated steam brings about the following changes in the composition of the residue:—

	Original oil.	After distilling off. 28·3%	After distilling off. 80%
Carbon	87·0	88·4	88·6
Hydrogen	11·0	10·5	10·1
Oxygen	2·0	1·1	1·3
Sulphur	—	—	—
Nitrogen	—	—	—

Notwithstanding the absence of sulphur, asphalt is readily formed from this oil, a fact which leads to the conclusion that sulphur is not an essential constituent of asphalt.

Moreover, the oxygen content of the residue shows no regular change. In no case do we find that the oxygen percentage increases with the asphalt content of the oil. This supports the view that oxygen compounds are also of no importance from the point of view of asphalt formation, an opinion which data given later will confirm.

The principal fact is the decrease of the hydrogen percentage, the significance of which, although pointed out by Berthelot, seems to have been overlooked. In Engler-Höfer we read: "While the volatility of the hydrocarbons increases with the hydrogen percentage, the least volatile hydrocarbons, especially the residues, must always contain the smallest percentage of hydrogen." The incorrectness of this view is obvious when we consider that the hydrogen percentage of all the olefines and naphthenes is the same for all molecular weights.

Generally speaking, however, the volatility of the members of a homologous series decreases with the increase in the number of carbon atoms in the molecule. (1) In the case of the paraffins: C_nH_{2n+2} as n increases the percentage of hydrogen falls. (2) In the case of the naphthenes and olefines C_nH_{2n} all members have the same composition—viz., C 85·7% H 14·3%. (3) In the case of the series C_nH_{2n-2} C_nH_{2n-4}, etc., the higher less volatile members have actually the higher hydrogen content. For the higher values of n the hydrogen percentage of all series approaches that of the olefin series.

In the case under consideration, then, we have a mixture of hydrocarbons with a hydrogen content far below that of the C_nH_2 series. If the distillation of this mixture were a purely physical process, then an increase of the hydrogen content of the residues might have been expected. But we find the contrary. From the physical point of view this distillation process must be considered merely as a separation of stable components. As a matter of fact, this process must be substantially a chemical process, or, more exactly, a decomposition. This point is of great importance. If the effect of the distillation of various hydrocarbon mixtures were only a separation off of the lower members of a homologous series, then the asphalt, as the residue, could only consist of hydrocarbons of very high molecular weight. But when we find that the distillation of these hydrocarbon mixtures must be regarded as a decomposition process it is no longer possible to maintain the view formerly held, which seems to be adhered to by all workers in this domain—a view which we also find expressed in the theories concerning the composition of coal.

Decomposition, on the contrary, leads, at least in the first phase, to simpler compounds. The fact that asphalt is formed by decomposition leads to an indirect determination of its composition. From the way in which the decomposition takes place we can draw conclusions as to the nature of the final product.

The Decomposition of Hydrocarbons.

In general we know nothing about the constitution of the hydrocarbons from which asphalt is formed, we know only that they contain carbon and hydrogen and various kinds of carbon links. When asphalt is formed one or more of these links must be broken up. The first question, therefore, is: Which of these links are broken down during the decomposition? Authorities generally are inclined to suppose a primary dissolution of the C-H bond (Berthelot, *Les Carbures d'Hydrogène*, 1901, Vol. III., chap. 2 and 3). This opinion is clearly formulated by Bone ("Coal and its Scientific Uses," 1919, p. 143). In general the C-C bonds are regarded as of great stability (*Holleman, Organische Chemie*, 1919, p. 51). An indication of the correctness of this view is afforded by a comparison of the heats of formation of the C-C and C-H bonds.

Further, an insight into the way in which the higher hydrocarbons may break up may be obtained by a study of the decomposition reactions of the simpler hydrocarbons, also from some reactions such as the formation of acetylene from carbon and hydrogen, the oxidation of the higher paraffins and the oxidation of asphalt base oils to asphalt.

The Heats of Formation of the C—H and C—C bonds.

The most probable values are (*Recueil Trav. Chim.*, Vol. XLI., p. 441):—

C — H bond	80 cal.
C — C (single)	70 „
C = C (double)	120 „
C ≡ C (triple)	160 „

The difference between these values is so slight, that no priori conclusions may be drawn therefrom as to the way in which hydrocarbons would break up.

The Pyrogenic Decomposition of the Simpler Hydrocarbons.

In this domain we have the researches of Haber (*Ber*, Vol. XXIX., p. 2694), Coward and Bone (*J. Chem. Soc.*, 1908, p. 1197), Lewis (*Proc. Roy. Soc.*, 1894, p. 91, 1895, p. 150), (*J. Chem. Soc.*, 1892,

p. 322, 1896, p. 226), Thorpe and Young (*Proc. Roy. Soc.*, 1873, p. 184), and Armstrong and Miller (*J. Chem. Soc.*, 1886, p. 74).

The systematic researches of Bone are particularly important as they have led to a new hypothesis relating to the decomposition of hydrocarbons which, with a little modification, gives an insight into the mechanism of the oxidation of hydrocarbons.

The researches of Bone deal mainly with two questions, *viz.* :—

(*a*) The hydrocarbons which are stable below 1200° C.

(*b*) The manner in which the decomposition of hydrocarbons takes place.

The first question can be answered with certainty. Methane is, below 1200°, the only stable hydrocarbon. An equilibrium can be established between CH_4, C and H_2 while all other hydrocarbons when the decomposition velocity is sufficient are converted into C and CH_4.

With regard to the second question, Bone, for example, showed that ethane does not decompose in the simple way via ethylene according to the scheme

$$C_2H_6 = C_2H_4 + H_2$$
$$C_2H_4 = CH_4 + C$$

but that it is probable that in this decomposition the groups CH_2 and CH which have a real but fugitive existence constitute the intermediate phase of the reaction. Bone gives the following schemes for the decompositions of ethane and ethylene :—

$$C_2H_6 = [2(=CH_2) + H_2] = \begin{cases} C_2H_4 \\ CH_4 \\ H_2 \\ C \end{cases}$$

$$C_2H_4 = [2(\equiv CH) + H_2] = \begin{cases} C_2H_2 \\ CH_4 \\ C \end{cases}$$

By this hypothesis of the formation of these very unstable compounds, many facts are explained. The formation of acetylene when methane is decomposed is also a support for Bones hypothesis. When we further consider the fact that the decomposition of methane leads to an equilibrium, we should be inclined to the belief that these groups have not only a fugitive existence, but that they play a part in this equilibrium. There are, however, some objections to Bones decomposition schemes. If we consider these schemes in connection with his view that the primary effect of heat is the elimination of hydrogen, together with a loosening of the bonds between the Carbon atoms, we arrive at the view that according to Bone's views the loosening of the C – C bonds depends

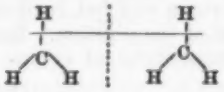
on the primary elimination of hydrogen. The old view as to the stability of the C—C bonds appears here very clearly, especially where Bone speaks of an elimination of hydrogen, but only of a loosening followed by a dissolution of the C—C bonds. Undoubtedly, on this point Bones hypothesis is not correct, as a primary dissolution of the C—H bond in the decomposition of ethane would lead in the first phase to the formation of butane, but no indications of such a change in the decomposition of this hydrocarbon are found.

It is very curious that Bone does not break away from the old idea of the stability of the C—C bonds, but holds the view that the formation of the CH_3 and CH groups depends on the primary dissolution of the C—H bond.

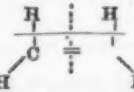
There are no reasons for this opinion, thermodynamic or otherwise, indeed, on the contrary, the facts indicate decomposition in another direction.

If we modify Bones scheme for the decomposition of ethane and ethylene by supposing a primary dissolution of the C—C bond and a secondary elimination of hydrogen from the so-formed one-C-atom groups, we find an easy explanation of the reactions. At the same time the connection between the stability of methane and the unstable character of the other hydrocarbons is cleared up.

Instead of Bones formula for ethane



and for ethylene



we suggest the following for ethane

$$\begin{matrix} C_2H_6 & \rightleftarrows & 2CH_3 \\ CH_3 & \rightleftarrows & CH_2+H \end{matrix}$$

and for ethylene

$$\begin{matrix} C_2H_2 & \rightleftarrows & 2CH_2 \\ CH_2 & \rightleftarrows & CH+H \end{matrix}$$

The nature of the decomposition products for ethane is determined by the groups CH_3, CH_2 and H which give as principal reaction products CH_4, C_2H_4 and H_2 with acetylene as a by-product formed by the decomposition of CH_2 groups into H and CH, the CH polymerising partly to C_2H_2. For ethylene we have the primary products CH_2, CH and H, which principally give acetylene and methane, the greater part of the hydrogen being used for the stable methane.

Methane is the only hydrocarbon without C—C bonds, and is also the only stable one. We differ thus in two points from Bones' hypothesis. (1) We disagree with the view that the pyrogenic decomposition of hydrocarbons commences with a dissolution of the C—H bond, and (2) we suggest that the existence of the CH_2 and CH groups, the intermediate products in Bones' hypothesis, is not only a fugitive one. Further evidence on this point is afforded by a consideration of the formation of acetylene at very high temperatures from hydrogen and carbon. As is well known, Berthelot formed acetylene by passing hydrogen over an electric arc formed between carbon terminals. The supposition that at so high a temperature a triple carbon bond could be formed directly is untenable. An easy explanation is given by the hypothesis that the primary reaction is the formation of CH groups, which are stable at these high temperatures but which when cooled polymerise to acetylene. This moreover supports the supposition that acetylene is generally formed by the condensation of two CH groups. At low temperatures the reaction $2CH \rightleftarrows C_2H_2$ passes almost entirely to the acetylene side, but it is still an equilibrium; so these CH groups must have a real existence even at low temperatures.

The phenomena displayed by the oxidation of paraffins and of asphalt base oils present an opportunity of elaborating these theories.

The Oxidation of Paraffins.

The principal researches in this field are those of Kelber and Grün (*Ber.*, 1920, 66, 1567 and 987). Their principal conclusions which our own work supports are:—

(1) Oxidation with elementary oxygen transforms the higher paraffin hydrocarbons into a mixture of fatty acids with about one-half the average number of carbon atoms in the molecule.

(2) The reaction takes place over a large temperature range.

(3) The reaction proceeds easily without the assistance of a catalyst.

(4) Oxidation with air or with a gas mixture of low oxygen content gives the same results essentially as with pure oxygen.

These reactions also indicate a dissociated condition of the hydrocarbon molecules, the dissociation products being oxidised by the oxygen to fatty acids. This view is supported by the following considerations:—

The lengths of the hydrocarbon chains differ from those of the fatty acids formed therefrom. This cannot result from a primary oxidation of the final CH_3 groups, followed by a gradual destruction

of the molecule until about one-half of the chain remains to form the fatty acids, the rest being oxidised to carbon dioxide and water. Actually, carbon dioxide is formed during the oxidation, but it can be limited to a very small quantity. Another objection to this view is that in the case of the primary oxidation of the terminal CH_3 groups the formation of alcohols, aldehydes and acids of high molecular weight would be expected, which would certainly not give an easy and almost quantitative yield of the lower fatty acids. A second possibility is that the chains are attacked in the centre but this seems improbable. There is no reason to suppose that the oxygen should specially attack the central CH_2 groups of the chains. As all the CH_2 groups in the paraffin hydrocarbons are equivalent, oxidation of these molecules would be expected to lead to the formation of all kinds of products, but on the contrary a definite reaction takes place.

We, therefore, conclude that this formation of fatty acids containing half the number of carbon atoms in the molecule must be preceded by a dissociation of the hydrocarbon molecules. This dissociation increases with the temperature. At 140° the dissociation of the higher paraffins leads to the formation of two about equal alkyl groups, which react with oxygen forming fatty acids. A connection between the pyrogenic decomposition of the hydrocarbons and the mechanism of their oxidation thus appears clear. In both cases the nature of the reaction products is determined, not by the hydrocarbons themselves, but by the very reactive groups formed by dissociation from the hydrocarbons. By help of this idea we can gain some insight into the oxidation of asphalt base oils to asphalt.

The Oxidation of Asphalt-Base Oils.

When paraffins are oxidised, oxygen is found in the residue, distillate and gaseous products. This is not the case with asphalt base oils.

The oxidation residues and distillates are found to be almost free from oxygen. In some native asphaltites appreciable quantities of oxygen are found, but this may be explained by the assumption that the basic oil from which these products were formed had a mixed-base character. Neither Engler or Abraham consider that oxygen is an essential component of asphalt, the latter holding that the oxidation process in the case of an asphalt-base oil is purely a dehydrogenation. As already mentioned we found that oxygen remains only to an inappreciable extent in the residue so that Marcusson's view on asphalt formation are obviously incorrect. At the same time it appears that the part played by the oxygen is quite other than that supposed by Engler and

Abraham. An insight into the reactions which take place when asphalt-base oils are oxidised to asphalt is obtained by studying the oxidation process at low temperatures, 200-275°, and especially by analysing the gaseous oxidation products. At these temperatures we find as the only oxidation products, with the exception of traces of formic and acetic acids, water, carbon monoxide, and carbon dioxide. The fact, however, that a chemical reaction has been started and that by this reaction at low temperatures, not only water but also carbon monoxide and carbon dioxide are formed, proves that Engler's and Abraham's views concerning the part played by the oxygen in this process are incorrect. An explanation of this process can be given by considering it in connection with the oxidation of paraffin.

While, in the case of the higher paraffins, we concluded from the study of the oxidation products, that a dissociation of the molecule into two approximately equal parts took place, in the case of the asphalt-base oils we arrive at an entirely different conclusion. In this case we must conclude that the splitting of the molecule gives rise to two very different portions, one of which contains only one carbon atom, which as the more reactive is readily oxidised.

The oxidation of asphalt-base oils, therefore, gives two kinds of reactions: (*a*) The oxidation of one-carbon-atom dissociation products; and (*b*) the regrouping of multi-carbon-atom dissociation products.

In solving the question as to which of these two reactions is characteristic for asphalt formation, we could eliminate the former if we could prove that the oxidation of the one-carbon-atom part resulted only in the formation of gaseous products. This should be the case if the one-carbon-atom groups were completely oxidised. Information on this point can be gathered from the relative proportions of the carbon and hydrogen in the gaseous oxidation products. We found for this proportion for different oxidations values between 1 to 4 and 1 to 10. A complete combustion of these one-carbon-atom groups would give values from about 1 to 1 up to 1 to 3. That the actual proportions found lie more to the hydrogen side, and the fact that CO is always found in the oxidation products prove that in the oxidation of asphalt-base oils we have an incomplete combustion of one-carbon-atom dissociation products of these oils which in every respect may be compared to the incomplete combustion of gases such as methane ethane, ethylene, etc. These reactions are always accompanied by the formation of carbon (carbon black industry). The same must, therefore, take place at the oxidation of asphalt-base oils, but in this case the carbon must appear in colloidal solution in the oil.

We therefore conclude that asphalt contains elementary carbon in colloidal form, and that this colloidal carbon is the essential constituent of asphalt. Confirmation of this view was afforded by further study on the asphaltenes and by the synthesis of asphalt from carbon and hydrocarbons.

Researches on the Asphaltenes.

In order to verify these theories it must first be proved that the asphaltic bodies have a colloidal nature.

The Tyndall effect is very clearly shown by solutions of the asphaltenes at dilutions of about 1 to 30,000. Ultramicroscopic examination shows good perceptible Brownian movement. On dialysation and ultrafiltration of these solutions the asphaltenes do not penetrate the membranes. This all shows that the different kinds of asphalt have a colloidal nature. This can be due either to very large molecules or to elementary carbon. If the colloid nature of the asphaltenes were due to high molecular complexity, we should expect to find asphaltenes of different chemical character, for it is hardly probable that in all cases the same high molecular weight body should be the cause of the colloidal nature. Now, although variations in the composition of the asphaltenes are stated to exist, no differences in their chemical behaviour have ever been found. They are all characterised by a highly indifferent nature, which is not influenced by the presence of elements other than carbon and hydrogen, *e.g.* sulphur. Only differences in the physical properties of the asphaltenes—*e.g.* their solubility—have been observed. This could be explained by the supposition that it is the different terms of the same homologous series which cause the colloid nature. The other view, *viz.*, that the colloid nature of the solutions of the asphaltenes is due to elementary carbon, is supported by the fact that these solutions always show a very dark colour. Most hydrocarbons are only slightly coloured; the same could be expected of their colloidal solutions, even of the highly polymerised ones. (The solutions of the highly polymerised hevea-rubber hydrocarbons are colourless.) The dark colour of asphalt solutions therefore indicates the presence of free carbon. The differences in solubility, moreover, cannot be ascribed to chemical differences, as the following research shows. Three kinds of insoluble dark products are distinguished, *viz.*:—

Asphaltenes, insoluble in benzine of low boiling-point, but soluble in carbon tetrachloride and in benzene.

Carbenes, insoluble in benzine of low boiling-point, and in carbon tetrachloride, but soluble in benzene. (Richardson, *J. Soc. Chem. Ind.*, 1905, p. 310.)

Free carbon insoluble in all solvents.

If we heat or oxidise asphalt, it is only at a high temperature that we have a rapid conversion of the asphaltenes into carbenes and free carbon. But if we heat the asphaltenes separated from these asphalts the conversion goes on much more easily. An asphalt, for example, which can stand a temperature of 350° for many hours without formation of notable quantities of free carbon gives asphaltenes which when heated for a quarter of an hour at 275° are converted almost totally into free carbon. As the purification of the asphaltenes is continued they become more and more sensitive to temperature and chemical influences. The purification of the asphaltenes may be effected in the following way: The product is very finely divided and extracted for many days in a Soxhlet apparatus successively with benzine 40°–60°, benzine 60°–80°, and mixtures of benzine 60°–80° and carbon tetrachloride. From time to time the asphaltenes are removed from the apparatus, dried at 130°, and again finely divided in a mortar. The extraction is continued until the spent solvent is practically colourless. These highly purified asphaltenes do not appear to be able to stand even this low temperature of 130°. By this purification they are partly converted into carbenes which carbenes in the same way, but with carbon tetrachloride as solvent can be transformed into free carbon.

If we assume a chemical difference between asphaltenes, carbenes, and free carbon, it would be necessary to infer a retarding influence of the medium on these reactions, which, considering the neutral character of the hydrocarbons, is quite impossible. From the colloid chemical standpoint the explanation of these phenomena is simple. Here we have no chemical conversion of asphaltenes into carbenes and free carbon. These asphaltenes remain unchanged through all these reactions. We have to deal here with a phenomenon well known to colloid chemists, *viz.*, that the removal of the protective bodies leads to a greater sensitiveness of the colloids.

The fact that there is no chemical difference between asphaltenes and free carbon is of great importance, for from this it follows that asphalt, at least as far as its essential constituent is concerned, belongs to another class of organic compounds, *viz.*, the coals. Indeed, when studying the constitution of coal, we immediately meet the same questions—is coal to be considered as a mixture of carbon and organic compounds or as consisting only of organic compounds? The former opinion was at one time generally held, but now the correctness of this view is contested, particularly by Franz Fischer, whose paradoxical remark, "Coal contains no carbon," is well known.

Essentially Franz Fischer's views are those which we have already combatted when considering the distillation, pyrogenic decomposition and oxidation of the hydrocarbons.

The proof advanced by Fischer that coal does not contain elementary carbon is valueless, since he merely bases this on the fact that continued extraction with solvents does not lead to a pure carbon residue. The purification of the carbon in this case, however, is impossible, owing to its very strong adsorptive properties, with which Fischer evidently did not reckon.

The further following considerations militate against the view that there is no elementary carbon in either asphaltenes or coal:—

(*a*) Many organic compounds, and especially the hydrocarbons, ordinarily exert, far below their boiling-point, a considerable vapour-pressure. If coal and asphaltenes consisted exclusively of organic compounds, it is strange that by the distillation of mineral oil, asphalt or coal tar, never a trace of asphalt or coal-like substance is found in the distillate.

(*b*) When asphaltenes are heated at 800° the hydrogen is not completely expelled. Nor can pure amorphous carbon be made by treating them with solvents. It is impossible that asphaltenes should stand temperatures of as high as 800°, considering that the stable methane decomposes with great velocity at that temperature. In these asphaltenes there must be therefore besides the hydrocarbons something else which prevents the decomposition of the hydrocarbons by stabilising the whole. This substance, which cannot be a hydrocarbon, must be carbon.

From a consideration of all these facts then we are forced back to the old conclusion that coal consists of elementary carbon and organic compounds, not in simple admixture in the ordinary sense of the word, but in the condition that the organic compounds are adsorbed by the carbon.

In direct connection with this, therefore, we hold that the formation of carbon attends the decomposition of organic compounds not only at high temperatures but also at all temperatures. The difference between various kinds of coal may be due to variations in the quantity and nature of the adsorbed compounds. The essential constituent is, however, elementary carbon.

It is evident that this adsorbent power of carbon will not be the same for all coals, and that differences in this respect may be the cause of great differences in the properties of various kinds of coal. The work of Chaney (*Trans. Amer. Electrochem. Soc.*, 1919, p. 91) is of special importance in this connection. Apart from any question as to whether there are two modifications of amorphous carbon, we may certainly assume a great influence of temperature on the adsorbing effect. Considering now in connection with Chaney's views our hypothesis that the essential constituent of the asphaltenes is colloidal carbon, this carbon, in view of the low temperature at which it is formed (600° being according to Chaney

the high limit for the formation of the active modification of carbon) must be of strong adsorptive power. We have seen that this is indeed the case, and that to this high adsorbent power the colloidal solubility of the asphaltenes is due. At higher temperatures we get an easier formation of the insoluble free carbon of less adsorptive power than the asphaltenes and therefore insoluble in all solvents.

The preceding theories were confirmed by a *Synthesis of Asphalt from Carbon and Hydrocarbons.*

We did not succeed in making asphalts by direct union of various carbons with protective bodies extracted from asphalts, but we did obtain good results by making carbon organosols by electrical dispersion of carbon, by which process the conditions of stability of these sols and the connection between asphalt and carbon organosols were cleared up.

(1) With carbon tetrachloride as medium. A dark grey solution is formed. The disperse phase goes through an ordinary filter. The solution is, however, not stable and separates after twenty-four hours.

(2) Carbon tetrachloride with 5 per cent. of an asphalt base oil as medium. The asphalt-base oil distillate had a light yellow colour and was free from asphaltenes. After ten minutes a perfectly stable brown colloidal solution was formed. If the process of dispersing carbon was continued for half-an-hour a grey-brown solution was formed, which after twenty-four hours separated a black precipitate leaving a stable brown solution.

(3) A mixture of carbon tetrachloride and protective bodies extracted from asphalt, as medium. The results were the same as in the former experiment, only the electrical dispersion of the carbon could be continued for a longer time before the grey sol was formed.

(4) Liquid paraffin as medium. A bluish-black solution was at once obtained, the disperse phase of which did not pass an ordinary filter. The filtrate was in this case almost colourless. For the formation of stable carbon sols, therefore, not all higher hydrocarbons can be used. We know scarcely anything about the composition and properties of these protective bodies, but think it likely that they generally have a highly unsaturated character.

(5) Asphalt-base oil distillate as medium. A brown solution is formed. Filtration through ordinary paper does not separate the disperse phase. The colour of the filtrate is, if the electrical dispersion is continued only for some minutes, brown with a green fluorescence, a colour often displayed by lubricating oils. The filtrate is perfectly stable. If the electrical dispersion is continued for a longer time the colour of the solution becomes very dark brown, as for more concentrated solutions of the asphaltenes.

After filtering off the large particles which are always formed by these dispersions, we obtain a dark brown solution from which the disperse phase is separated by benzine 40–60.

Analysis of the disperse phase gives C 86·7 per cent., H 7·5 per cent.

From a comparison of the above results we can draw the following conclusions. By the electrical dispersion of carbon in various organic liquids we obtain grey-black and brown colloidal solutions. The brown solutions are stable, the grey not. The brown sol is obtained if we either add protective bodies to the medium or disperse the carbon in a medium of asphalt base oil in which the presence of these protective bodies may be expected. That these brown sols are formed from carbon and protective hydrocarbons and not by decomposition of the medium is most probable.

In the first place no decomposition at all is observed when taking liquid paraffins as medium; it is improbable that the asphalt base oils should show marked differences in stability compared with the liquid paraffins. In the second place, taking carbontetrachloride as medium we obtain in the first place a grey sol, but after adding protective hydrocarbons to the medium we obtain a brown sol. If decomposition of the protective compounds were the cause of this brown colour, then a mixture of grey and brown sols might be expected. From these considerations it follows that decomposition reactions play no part in the process, but that when carbon is dispersed electrically in an asphalt-base oil distillate medium, a disperse phase is formed by carbon from the electrode stabilised by the protective hydrocarbons present in the oil. This disperse phase has all the properties of the asphaltenes and a similar chemical composition, so that we can really speak of a synthesis of asphaltenes from carbon and hydrocarbons. The asphaltenes formed by electrical dispersion differ only in one respect from ordinary asphaltenes in that they are less stable. But this is to be expected, since at the moment of electrical dispersion particles of very different sizes and adsorbent powers are formed, and so the conditions for the formation of stable sols are much more favourable in the ordinary methods of asphalt formation.

If oxygen is led into an asphalt base oil distillate unsaturated hydrocarbons and very finely divided carbon are simultaneously formed, so that we then have the most favourable conditions for the formation of stable sols.

The same difference of stability is noted in the case of the metal hydrosols formed by electrical dispersion and those formed by the reduction of metallic salts in presence of a protective body. Asphaltenes made from asphalt-base oil distillate by distillation or oxidation may be compared to the more stable metallic colloids made by reduction of metallic salts.

The results of the preceding experiments, *viz.*, the synthesis of asphalt-like substances from hydrocarbons and carbon is of significance, not because it is an unassailable determination of the constitution of the asphaltenes, but because it is the last link in a chain of arguments which lead to the view that solutions of the asphaltenes are to be considered as very stable carbon oleosols. This stability is due to the extremely favourable conditions of formation, namely :—

(1) The low temperature at which the carbon formation takes place, the resulting carbon thus having very strong adsorbent properties.

(2) The finely divided state of the carbon.

(3) The great excess of protective hydrocarbons surrounding the carbon at the moment of its formation.

The Prevention of Emulsions.

By A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.

The rising value of crude oil, and the increasing attention to economies and conservation, are forcing upon oilfield operators closer attention to every form of waste. Emulsions have always constituted one of the most serious forms of waste upon which little research has been undertaken either towards their prevention or destruction until recent years; but even now, with our advanced knowledge concerning their origin and methods of breaking down, there are still heavy losses sustained in ignorance or disregard. The subject has attracted renewed interest in view of the studies undertaken by the Washington Bureau of Mines and described in some detail by Swigart and Beecher.*

Obviously it is preferable in every case to avoid troubles rather than prescribe remedies. Emulsions form under certain widely differing but nevertheless restricted conditions, which are approximately known. Some types of oil are more liable to emulsify than others, but whether of light or heavy density, of asphaltic, naphthenic, paraffinous or mixed base, most oils are known to form emulsions under certain conditions. The forms of emulsions are as varied as the conditions that promote their formation. One point does, however, appear to be reasonably certain—viz., that they are rarely if ever formed in the earth itself, except perhaps within the immediate vicinity of actively producing or flowing wells. Until the operator himself provokes subterranean disturbances and movements, emulsions are probably non-existent.

As the admission of water to the well is the primary cause of emulsions, its isolation will effect a remedy. Unfortunately, the sources of water admission cannot always be traced, or, if located, cannot always be attacked in a useful manner, through the antagonism of competing interests who might suffer permanent or temporary loss of production whilst operations for its exclusion were being conducted. But quite apart from water admission due to culpable negligence or injudicious work, it is impossible in many fields to avoid the entrance of water into the oil-sands when the gas pressure has been released, and the strata are faulted and fissured, and, perhaps, loosened by the removal of large quantities of sand in unconsolidated sediments. Then, again, where synclinal

* Manual for Oil and Gas Operators, Bull. 232, Bureau of Mines, Washington.

or edge water encroaches on a field, large quantities of oil would have to be abandoned unless operators were prepared to extract a mixture of oil and water for some time after the appearance of the water. At other times water occurs in the oil-sands themselves, or separated by so thin a parting that its isolation is virtually impossible, and a mixture of oil and water has to be extracted, as in the El Dorado field of Kansas.

From oilfields like the coastal belt group of Mexico, the Baku of Russia, and the Kern River of California, the oil dregs are being rinsed from the beds by water, which is largely instrumental in sustaining the yield of these areas, even if it imposes expense and difficulties on the producer. In the case of Mexico, the oil dregs are being stripped from cavernous limestones which are being rapidly invaded by rising water; whilst in the other cases no practicable scheme could be evolved, even if desirable, to exclude water which enters through all kinds of obscure channels, often perhaps unconnected with the developments by man.

So called oilfield emulsions or "cut oil," as is well known, vary considerably in their constitution. Some are exceedingly refractory; others readily submit to treatment. One variety will gradually break down if left in flat vessels and subjected to a moderate increase of temperature. Another type cannot be broken down by moderate heat or settlement. Some are peculiarly susceptible to electrical treatment; others require repeated retreatment or preliminary heating. Most observant oilfield operators have noticed that emulsions appear and disappear in wells in a way that indicates that the critical conditions for their production are not constant. At one speed of bailing, swabbing, pumping or flowing, a particular well may yield emulsion, when at another an oil-water unemulsified mixture will be expelled or extracted under very variable conditions. Recent American investigations have shown to what extent emulsions can be avoided by attention to numberless mechanical and often trivial details. By careful adjustment of the rate of flow, or extraction, control of pressure, and condition of plant many troublesome emulsions with their costly treatments and delays can be avoided.

Occasionally the disappearance of emulsions can be directly traced to a diminished influx of water following the retention of pressure, instead of permitting uncontrolled flow, but often no material change in the oil-water ratio results from controlled pressure, and the change is undoubtedly due to the diminished inflow of gas. As agitation is largely instrumental in producing emulsions, anything tending towards its diminution is likely to be helpful.

There is abundant evidence to show that emulsions are formed in the wells, and often in the mechanical appliances used for pro-

duction. A faulty cup or plunger in a pump, or even a scored or bruised ball valve or seating is sufficient at times to cause emulsions. Under the high pressure of 500 to 1000 lb. pressure per sq. in., which is a common pressure reached at the pump in deep wells, the slightest slip or leakage would cause a pulverisation particularly favourable for the production of emulsions if water were present as well as finely divided inorganic particles. The appearance of so-called "cut oils" is often a sure indication that the pump needs attention.

Emulsions, however, are common even where wells are allowed to flow freely, their formation being due to the fierce agitation by gas of a mixture of water and oil and inorganic particles within a confined space. Controlled or regulated intermittent flow may prevent their formation by diminishing the influx of gas, and perhaps sediment, and so promoting calmer conditions in the casing. Emulsification is often effected through obstructions in the path of flow setting up a lively agitation. Such emulsions have been repeatedly traced to their seat of origin beyond which the water and oil freely separated on settlement.

The attachment of flow nozzles often causes emulsions, and they have been overcome at times by introducing between the nozzle and the flow-pipe an enlarged cylindrical vessel where the water can separate and be drawn off by a trap.

Amongst other ways of avoiding the formation of emulsions is adding water or oil to wells to maintain a head which could not be sustained when steadily pumping. A still better plan, when feasible, is to have two pumps, one to draw from the bottom of the well and the other some distance higher. In this way the speeds of the two pumps can be adjusted so that the lower pumps mainly or entirely water, whilst the higher discharges nearly clean oil. The same procedure can be adopted with air lifts where emulsions are very liable to form on account of the energetic agitation set up in the rising main. An improvement can often be effected by attaching a long gas anchor to the pump, thereby deflecting the gas into the casing instead of through the pump barrel in company with the oil.

The position of the pump in the well is often a factor which determines the amount of "cut oil." When there is a high static and working head of fluid, emulsions can often be entirely avoided by keeping the pump barrel high up in the fluid and permitting to remain in the well a fairly heavy column of water, which, whilst acting as a sedative on the gas, does not prevent the free admission of oil.

Those engineers acquainted with the Russian oilfields know how restricted were the conditions for the avoidance of emulsions. Only by a careful adjustment of top and bottom bailings, size of

bailer, and speed of running, could emulsions be avoided in many Baku wells yielding 500 to 1000 bls. daily mixed with much water.

It would be of general value to the industry if members of the Institution would send records of any experiments in emulsion suppression, or observations connected with their occurrence, as the subject can only be intelligently pursued by an accumulation of facts bearing on the problem.

The Berginisation of Coal and Oil.

By Alfred W. Nash, M.I.Mech.E.

Some twelve years ago Dr. F. Bergius commenced research work on the artificial production of coal, and during the last twelve months much has been heard in this connexion, both in papers read before the Institution and elsewhere, and also in regard to the production of oil from coal and the hydrogenation of mineral oils.

A number of experiments have been performed in the past by various workers to obtain synthetic coal from wood and similar material by the application of heat and pressure, but all have failed, due to the formation of coke lacking in hydrogen, brought about by the exothermic character of the reaction, which renders control of the temperature impossible.

Bergius decided to carry out similar experiments in water in a high pressure bomb, thus providing a means of absorbing the heat produced and so eliminating tne danger of super-heating and enabling the temperature to be kept below 340° C.

Cellulose was heated in the bomb up to about 340° C. under a pressure of 200 atmos. for a period of twelve hours, and a black amorphous mass was obtained which, on analysis, proved itself to be composed of 84 per cent. carbon, 5 per cent. hydrogen and 11 per cent. oxygen, a quantity of CO_2 being formed at the same time.

It was found that decomposition of the product set in when the temperature went above 340°.

Bergius called this reaction product "Endkohle" and illustrated the reaction by the equation $2C_6H_{10}O_5 = 2CO_2 + 5H_2O + C_{10}H_{10}O$.

From the many results obtained at varying temperatures and periods of reaction, Bergius worked out a coefficient of velocity change from which he calculated that the formation of natural coal has taken about ten million years.

Upon experimenting further with a small hand cylinder fitted with a piston, in which Bergius claims to have raised the pressure

to 5000 atoms., it was found, when maintaining this pressure for sixty-four hours at a temperature of 180°, that the carbon content of the "endkohle" increased to 88 per cent. and a gas was formed which contained 80 per cent. of CH_4.

Bergius then decided to carry out the treatment in presence of hydrogen in the hope that hydrogenation would take place with the formation of a liquid product.

The synthetic product, "endkohle," was therefore placed in a bomb together with hydrogen and heated to a temperature of 400° C. at a pressure of 100 atmospheres, and Bergius found that 70 per cent. of the product could be extracted with benzene, the extract being similar in appearance to a normal mineral oil.

This discovery led to a number of further experiments, but the difficulty of coking, mentioned earlier, necessitated steps being again taken to eliminate super-heating. This was done by mixing the coal with oil, and the work then proceeded apace, but with natural coal as the original material.

Bergius claims to have achieved the liquefaction of natural coal up to about 90 per cent., calculated on an ash and water-free basis.

The Hydrogenation of Oil.

Bergius then turned his attention from the hydrogenation of coal to the hydrogenation of heavy mineral oils.

Everyone is now familiar with the process of cracking, but the few successful cracking plants in use are much more successful in their operation when comparatively light "cuts," such as gas oil, are used as the original material.

The poorer an oil is in hydrogen, or the richer in carbon, the greater the amount of carbon deposited when cracking takes place, and this carbon deposition is the great stumbling-block to all the present known commercial methods when heavy oils are used.

Bergius claims to hydrogenate such crude oils as do not pay for refining, such as Panuco crude, and also the residues from other oils which at present cannot be cracked, owing to the carbon trouble, into light hydrocarbons without the formation of carbon and with small gas losses.

That the process has got beyond the laboratory stage is proved by the fact that the present works employ some 250 men, of whom about 30 are University trained engineers and chemists, and some 40 skilled mechanics: the works, which are situated at Rheinau, on the Rhine, near Mannheim, are equipped with railway sidings and a waterway connexion to the Rhine.

When a fresh oil is to be treated, it is first of all experimented with in a small autoclave, having a capacity of about five litres.

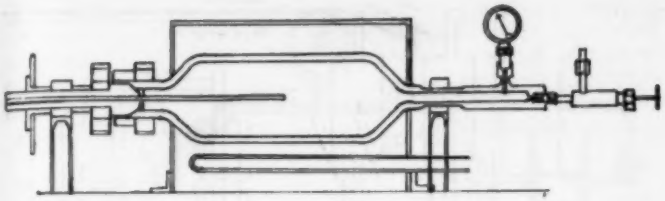


FIG. 1.

As will be seen in the sketch, Fig. 1, this autoclave has an opening at one end through which the oil can be admitted to the cylinder; through the cover of this opening projects a thermometer pocket. The other end of the cylinder is drawn down and carries a pressure gauge fixed to a branch piece, and at the end is a connexion for a gas cylinder.

Heat is applied by means of a gas burner, the heated portion of the bomb being surrounded by a lagged cover. The whole autoclave revolves in bearings at about 45 r.p.m., being driven by a sprocket wheel from a countershaft overhead.

A measured quantity of oil is introduced into the autoclave and the end sealed. Hydrogen is then pumped in to a given pressure and the gas inlet is sealed. The contents are then raised to a temperature of between 350° and 400° C., and kept at this temperature for about an hour, the autoclave revolving during this period.

It is stated that on first heating the pressure increases, then gradually falls off and eventually remains constant. The reason given for the falling off in pressure is that the hydrogenation process has commenced.

The autoclave is then cooled, the gas analysed and from such analysis the quantity of hydrogen absorbed is computed. The product is then withdrawn and fractionally distilled. It is claimed that an oil is recovered more mobile, greater in volume and with a lower average boiling point than the original.

The next step is with the large scale plant. This consists of an autoclave 3 feet inside diameter by 30 feet long, fitted with a dephlegmator at one end 30 feet high; a stirrer rotates throughout the whole length of the autoclave.

Fig. 2. shows a diagram of the plant. Oil is pumped in on the left, through a preheater 1 to the autoclave 2.

The hydrogen is pumped in on the right through a preheater 3, and thence to the autoclave where the oil and hydrogen mix, and cracking and hydrogenation take place simultaneously.

The vapours pass, together with the circulating hydrogen,

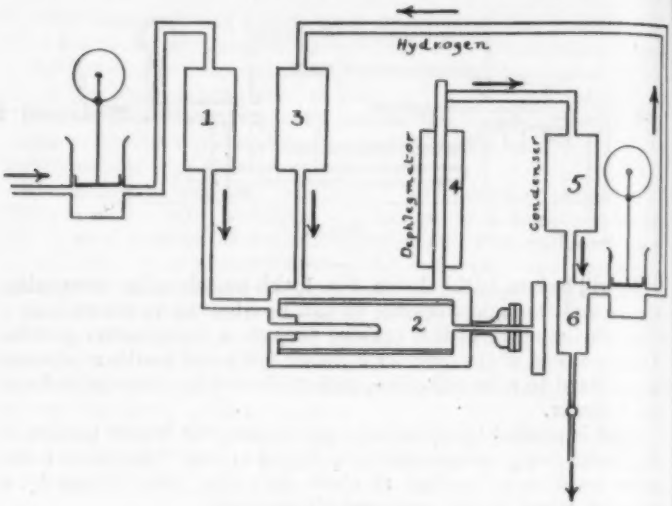


FIG. 2.

through dephlegmator 4 to the condenser 5, the distillate being collected in receivers 6 and the hydrogen and any permanent gas formed is pumped back into the autoclave again.

The receivers 6 are mounted each on a separate weigh-bridge, which indicates as soon as these are full, when they are cut out of the circuit and emptied.

By means of an outlet near the bottom the system is made continuous, and it is claimed that the plant can work for months on end without closing down, due to the absence of carbon formation.

The quantity of hydrogen absorbed is taken as that portion represented by the difference between the quantity of gas at first put in and the quantity remaining in the circuit.

A point which will at once arise in the mind of the chemical engineer, apart from the mechanical efficiency of the plant, is whether the porosity of the cast steel autoclave has been taken into account in this calculation.

That this point has evidently been considered by those responsible is borne out by the fact that a recent patent calls for a double autoclave, the inner shell containing the oil and hydrogen and the annular space between inner and outer shell holding an inert gas at a pressure equal to the pressure inside the cracking chamber proper.

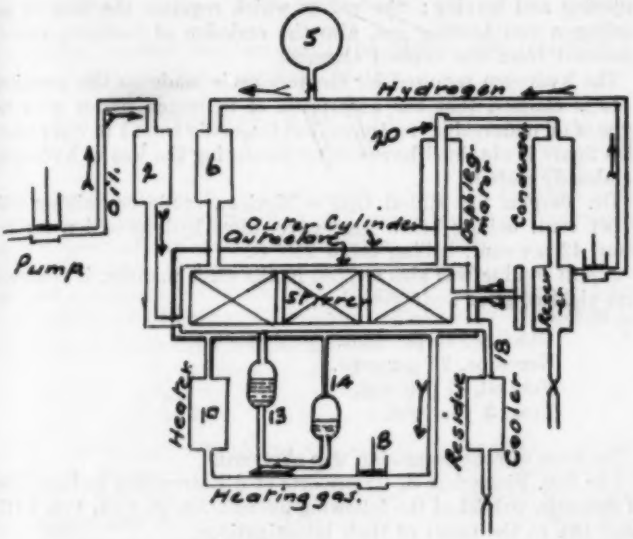


FIG. 3.

Fig. 3. will explain this more fully.

The inert gas referred to has been made to act also as the heating medium.

Oil from the feed tank is pumped through preheater 2 and thence to the inner vessel. The hydrogen receiver 5 emits hydrogen through preheater 6, also to the mixing chamber.

The heating gases are circulated through the annular space, and returned by pressure pump 8 through heater 10 to the pressure jacket continuously.

Any slight difference in pressure between the inner and outer shell is indicated by the water column 13, 14. The vapours and hydrogen are led away through pipe 20 and treated as described previously and the residuum is drawn off through pipe 18.

The plant at present in use is capable of handling 50 tons of oil per day, but great care has to be taken to prevent accidents. Whilst the plant is in operation no workman is allowed inside the building.

All pressure and temperature recording is done, by the application of electricity, in a separate control room. Continuous charts are drawn by recording instruments showing the temperature and pressure both inside and outside the cracking chamber, the temperature of the oil and hydrogen and of the heating gas, both on

entering and leaving; the valves which regulate the flow of oil, hydrogen and heating gas, also the emission of residues, can be operated from the control chamber.

The hydrogen required for the process is made on the premises.

It is claimed that the absorption of hydrogen varies with the type of oil undergoing treatment, but is usually from 1 to 2 per cent.; this figure is obtained, however, by measuring the loss of hydrogen, as already stated.

Dr. Bergius has stated that a Mexican crude containing only 5 per cent. boiling below 210° gave, after hydrogenation for one hour, 42 per cent. boiling below 210° C.

A still residue was also treated in the same manner, it is stated, and yielded, after hydrogenation,

Gasoline, 45 per cent.
Kerosene, 25 per cent.
Fuel oil, 27 per cent.
Loss, 3 per cent.

No trace of coke formation was observed.

The Soc. Financiere de Transports et d'Entreprises Industrielles, of Brussels, published the following information (*S. C.* 1, Vol. VIII., page 18), as the result of their investigations.

"The Berginisation of a heavy oil yields 30 per cent. of light spirit, 30 per cent. of fuel oil, 30 per cent. Diesel oil, and 10 per cent. gas. The quantity of hydrogen required is approximately 1 per cent. for heavy oils, 2 per cent. for liquid tar, 3 per cent. for coke-oven tar, and 4 per cent. for coal."

There seems to be little doubt that, as regards oil hydrogenation, the Bergius Process is a proved commercial proposition, and as the demand for light boiling products increases, a greater margin for profit will be assured. Details as to coal treatment, however, are less clear. The nature of the coal itself will be the determining factor, and in this connexion, it is probable that German coals, which are mainly lignitic in character, will be more suitable for Berginisation than the majority of English, Scotch or Welsh coals.

The main difficulty would appear to be the heavy capital outlay required on the plant. It has been estimated that the capital cost of a plant to deal with 100 tons of oil per day is in the order of £160,000, but that working costs show a good profit even on this outlay.

The importance of the discovery will be evident in this country, where free oil on a large scale has still to be found, but where huge deposits of coal suitable for hydrogenation exist.

Some further Studies with the Moore Spontaneous Ignition Meter.

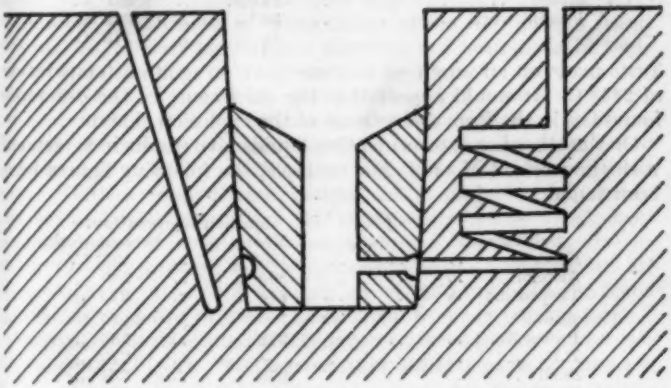
By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven.

The present note refers to experiments which had for their initial object an inquiry into the effect of "anti-detonating" compounds on the spontaneous ignition temperature of fuels.

As a standard, liquid heptane was selected as having a similar ignition temperature to petrol and because it can be brought to a very high state of purity. The pure heptane used in most of the following work had the following characteristics :—

d 20°/40° C.	=	0·6835 (in air)
b.p.	=	98·4° C.
$n_D^{\sim}$ 20° C.	=	1.3877

The ignition meter employed was similar to the instrument used by Moore (Journ. Inst. Petr. Tech., VI., No. 22, p. 189) with the exceptions that two spiral tubes in parallel are provided for heating the oxygen, and the ignition chamber is of greater capacity—38 cc. as compared with 24 cc. calculated from the dimensions of Moore's crucible. A section of our ignition chamber is shown in Fig. 1., which also shows a loose steel block in place, which was sometimes employed to reduce the volume of the ignition chamber. With the block in, the volume of the chamber was 16 cc.



FIG

The oxygen was prepared by the electrolysis of strong KOH solution, using a nickel anode. Any ozone formed would undoubtedly be decomposed in passing through the heated spirals. No attempt was made to dry the oxygen, but coming from a strong potash solution the amount of moisture would not be excessive.

The temperature of the block was determined by means of an accurately calibrated copper-eureka couple, employing the usual precautions of keeping the cold junctions in a Dewar vessel in water at 15° C., ice not being available. The potentiometer employed permitted the e.m.f. developed by the couple being read to 0·01 millivolts, corresponding to about 0·2° C. For the control of the temperature it was found more convenient to use a mercury thermometer, the error of which was determined by using it side by side with the thermo couple.

A gas ring burner was used for heating the block, this giving a more even heating over the base of the block than a Bunsen burner.

Initial experiments showed that variation of the oxygen speed from 12 cc. to 40 cc. per minute made no difference to the ignition temperature of heptane. The explosions produced appeared to become somewhat more vigorous with increasing oxygen speed. In general a speed of 20–25 cc. oxygen per minute was employed.

The ignition temperature found for pure heptane was 245° C. This is 36° lower than the temperature found by Moore. In order to find if the difference arose from the somewhat greater explosion chamber, tests were made with the steel block inserted. The results may be set out as follows:—

	Chamber volume.	Ignition temperature.
Moore	24 c.c. ..	281° C.
Present work	38 „ ..	245° C.
	16 „ ..	278° C.

Tests made on an unrefined heptane gave an ignition temperature of 244° C. It would appear that the chief cause of the difference found lies in the form and volume of the explosion chamber.

On the other hand, tests on other liquids give results in agreement with the work of Moore. For example, the following figures have been found:—

Substance.	Ignition temperature. Moore.	Present work.
Ether	190° C. ..	196° C.
Alcohol	395 „ ..	385 „
Turpentine	274 „ ..	275 „
Petrols:—		
Pratts No. 1	272 „ ..	285 „
B.P.	— ..	279 „
Shell	279 „ ..	284 „
Shale	— ..	278 „
Kerosene (White Rose) ..	251 „ ..	257 „

Turpentine is of especial interest in that Moore found the same ignition temperature in oxygen and air. Tests were therefore carried out, using air instead of oxygen in the case of this body. It was found extremely difficult to determine the ignition temperature, as the explosions became fainter and fainter as the temperature was lowered. It appeared, however, to be of the order of 284° C.

Experiments were made to determine the effect of adding 1 per cent. of carbon tetrachloride or chloroform to petrols. It was found that the ignition temperatures increased by 1° C. The following results were obtained with additions to pure heptane :—

Substance added gms. per 100 c.c.	Ignition temp.	Change.
Nil	245	—
m-Xylidine	261	16° rise.
p-Toluidine 1·0	259	14° „
Dimethyl aniline 1·0	251	6° „
Water 50 (?)*	249	4° „
Ammonia (saturated)	246	1° „
Lead tetraethyl 0·25	231	14° drop.
Lead tetramethyl 0·25	236	9° „

* 1 drop of water was introduced into chamber with 1 drop of heptane.

The foregoing results show that the addition of anti-detonating agents does not affect the ignition temperature to anything like the extent of their effect in an engine.

In all the foregoing work, the "wait period," *i.e.*, the interval between the introduction of the fuel and the resulting explosion, was of the order observed by Moore. No systematic variation of the wait period appeared to arise from the experimental variations other than excess of temperature above the ignition point. Figures for the wait period have therefore not been given in these notes.

The question of the action during wait period seemed to call for further experimental investigation, and attempts were made to examine the temperature variations in the explosion chamber in the course of carrying out the determination of ignition temperatures. With a small thermo couple and a portable indicator it was certainly observed that the introduction of the fuel drop brought about a lowering of temperature followed by a rise in which the temperature of the gaseous mixture might attain an indicated 30° C. above the temperature of the block. The mixture then either exploded or cooled down again to block temperature.

After various attempts the experimental arrangements took the form shown in Fig. II. The temperature indications in the interior of the explosion block were given by means of a thermo junction of 34-gauge copper and eureka wire developing 1 millivolt per

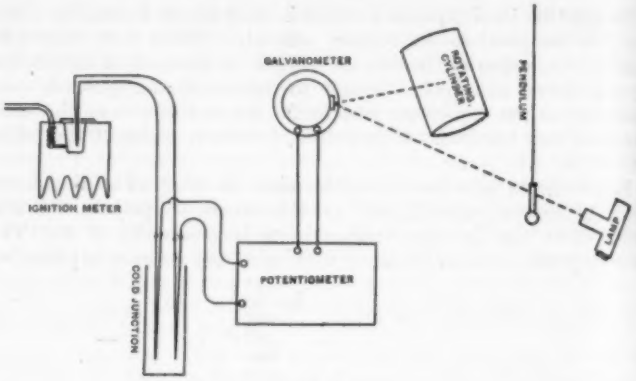


FIG. II.

17° C. at 245° C. The e.m.f. developed was balanced by the potentiometer.

The rotating cylinder carried a sheet of photographic paper and recorded the movement of the spot of light from the galvanometer. A seconds pendulum before the lamp broke up the trace into dashes, and thus gave a time scale.

Fig. III. (*a*) to (*e*) was prepared from typical photographic charts obtained. Taken in order these show :—

(*a*) 4° *below ignition point.*—The temperature falls on introduction of fuel and then rises slowly to temperature of block.

(*b*) *Just below ignition point.*—After the initial cooling the temperature rises well above that of block and then falls off again.

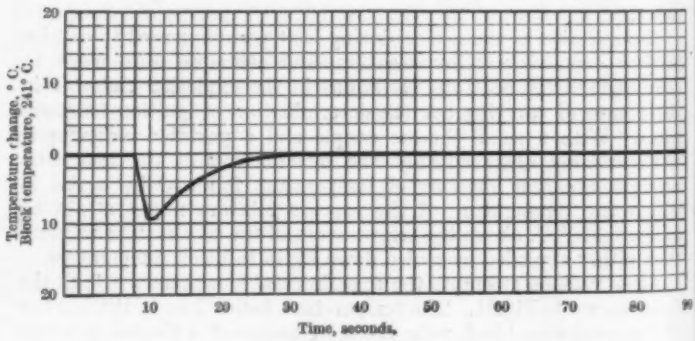


FIG. III. (A).

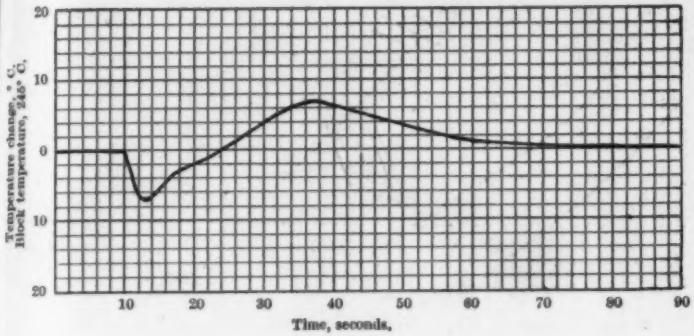


FIG. III. (B).

(*c*) *Ignition point.*—After a lag of 17 secs. the temperature is rising rapidly and the explosion occurs.

(*d*) 1° *above ignition point.*—The lag in this experiment has increased somewhat (24 secs.). The curve shows a very common occurrence—a secondary explosion. After the first explosion the mixture burns at the hole in the cover, and after a few seconds the flame strikes back, giving a second explosion.

(*e*) 27° *above ignition temperature.*—The lag here is only some 4 secs., and the explosion appears to occur before the gaseous

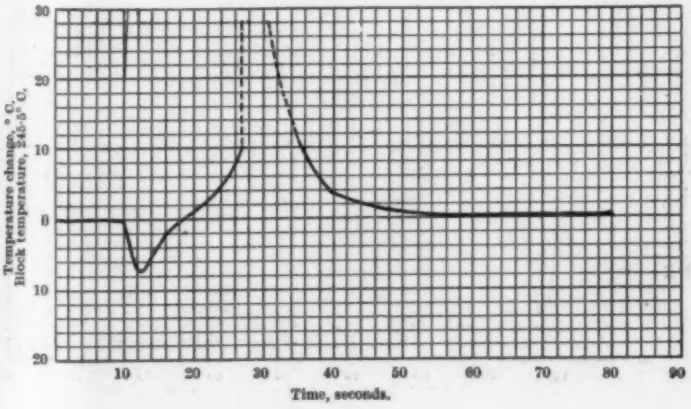


FIG. III. (C).

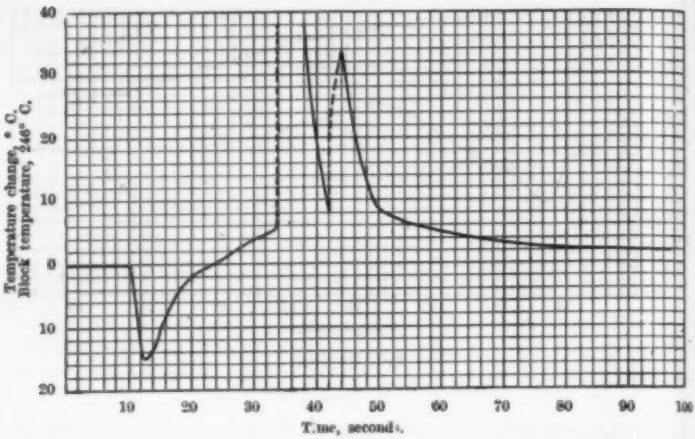


FIG. III. (D).

mixture has heated up again to the temperature of the block. This is without doubt due to inertia of the galvanometer coil and lag of the thermo couple. It must be borne in mind that in all cases the indicated changes of temperature are probably very much below the truth.

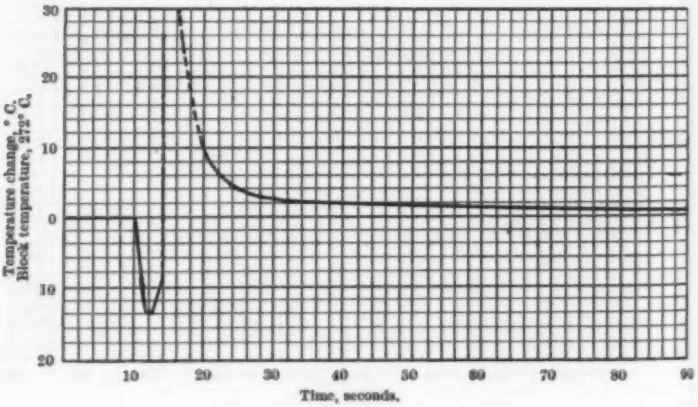


FIG. III. (E).

The foregoing experiments show very clearly that in the wait period before spontaneous ignition an exothermic reaction between the fuel and oxygen is proceeding, and that probably when this reaction attains a sufficient velocity it initiates the ignition and explosion.

Some clue as to the nature of this initial reaction was afforded by a further experiment in which oxygen saturated with heptane at air temperature was drawn over 100 g. of iron tacks contained in a silica tube 2½ cm. diameter. The tube was electrically heated and the exit gases tested by bubbling through suitable solutions. It was found that at from about 5° below the ignition temperature distinct quantities of carbon dioxide were formed, and the amount increased with rise of temperature. No organic acids or aldehydes were traced. It is of interest to note that up to temperature 40° C. above the normal ignition temperatures, as found by the block, no ignition of the gases took place.

Apparently the initial reaction which, in the block, leads to ignition is the complete combustion of a portion of the fuel, though no doubt there are intermediate stages in the oxidation depending on the type of fuel used. It may be mentioned finally that some experiments were made in the block with alcohol and temperature variation curves were obtained very similar to those obtained with heptane. It was therefore not thought worth while to do much in this direction because of the lack of any characteristic differences in the curves obtained.

This work may be regarded as a further portion of the extended investigation which is being carried out on the physical properties of pure and mixed fuels at the joint request of the Distillers Company Limited, and the Fuel Research Board of the Department of Scientific and Industrial Research. We wish to take this opportunity of recognising the financial assistance rendered by them towards the expenses of this research.

The Effect of Thermometric Lag in Engler Distillation.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven.

In the following work the thermometers and other apparatus employed were of the dimensions adopted by the Standardisation Committee of the Institution of Petroleum Technologists.

The fact that mercurial thermometers are affected with a large lag is readily seen if a cold thermometer be suddenly immersed in the vapour of a pure liquid. The following table shows the effect of plunging a thermometer into steam in the one case and heptane vapour in the other case. In this and succeeding experiments the usual distillation apparatus was employed and the rate of distillation adjusted to be 2 drops per second, except in the case of the first steam experiment where a steam can was used.

Table 1.

Time.	Water.		Heptane.	
secs.	Temp.	Lag.	Temp.	Lag.
0	20·0	—	20·0	—
10	98·4	1·1	95·5	2·3
20	98·8	0·7	97·1	0·7
50	99·0	0·5	97·3	0·5
100	99·1	0·4	97·4	0·4
200	99·3	0·2	97·7	0·1
400	99·4	0·1	97·8	nil
800	99·5	nil	97·8	nil

There appears to be but little true difference in the lag in two cases, in spite of the fact that in the case of the steam there were specially favourable conditions—namely, an almost unlimited supply of vapour of high latent heat of condensation.

In order more closely to study this question of lag, experiments were made with a number of thermometers. These were as follows:—

D	Ordinary A.S.T.M.
243,137	Specially made to minimum dimensions of specification.
243,133	Specially made to maximum dimensions of specification.
244,381	Specially made with thick walled bulb.
102	A.S.T.M. standard American manufacture.
23,250	A.S.T.M. standard English manufacture.
4, 6, 13	Enclosed scale A.S.T.M. German manufacture.

For the loan of the last five thermometers we are indebted to Mr. Kewley.

Water or heptane was distilled from the Engler apparatus, and when a steady rate of 2 drops a second was attained the thermometer under test was plunged into position and a stop watch

started. When the thermometer reached a given higher temperature the watch was stopped. The thermometer was removed and allowed to cool down again to room temperature. The experiment was then repeated for the same or another upper temperature. In this way the curve of rise was obtained for all the thermometers. The steady maximum temperature indicated was also noted for each thermometer. Calling this last temperature T and the temperature indicated after a time t being called θ it appeared to be a reasonable hypothesis to write, following Newton :—

$$d\theta/dt = k\,(T-\theta) \qquad \ldots\ldots\ldots\

The results are tabulated below, and Fig. 1 shows the experimental points for thermometer 243,137 in the vapour of three different liquids:—

TABLE 2.

Thermo.	k. Water.	Heptane.	Ratio. k heptane/k water.
D	0·69	0·36	0·53
243,137	0·72	0·41	0·57
243,133	0·58	0·30	0·52
244,381	0·36	—	—
102	0·51	0·30	0·59
23,250	0·53	0·28	0·53
4	0·43	0·37	0·86
6	0·39	0·33	0·84
13	0·49	0·41	0·84

No. 244,381, which was made with a thick walled bulb, it will be noticed is the slowest. Unfortunately it was broken before the speed in heptane vapour was determined.

The constant k is higher in steam than in heptane vapour, and the ratio appears to depend on whether the thermometer is of the enclosed scale or solid stem type.

Equations very similar to those given above have been suggested by Thiessen, Vergleichungen von Quecksilber Thermometer. Metronomische Beträge Berlin No. 3, 1881. These are quoted by Chwolsen, Traité de Physique, Vol. III., p. 45.

It is possible that the last slow rise of a thermometer to equilibrium is dependent more on the heating of the stem and consequent expansion of the mercury thread than on the passage of heat into the bulb. For the last few tenths of a degree rise, therefore, the logarithmic law may not hold quite exactly. With the type of thermometer being considered, however, the variation, if any, will be quite unimportant.

That the constant k depends on the latent heat of evaporation of the liquid in which the determination is made is shown by the following results on thermometer 243,137 in three liquids.

TABLE 3.

Liquid.	k.	Latent heat. cals./gm.
Heptane	0·41	76
Alcohol	0·50	207
Water	0·72	539

It was seen that this thermometric lag must effect the temperature readings in Engler distillation, and a series of experiments were carried out to determine the magnitude and distribution of the error from this cause in such distillation.

In order to obtain temperature readings practically free from lag copper-eureka thermo couples of 26-gauge wires were employed.

The junction was arranged as shown in Fig. 2 in order to prevent the junction being cooled by the trickling down of liquid condensing on the higher parts of the thermo couple. The positions in the neck of the standard flask of the junction and thermometer bulb are shown in the diagram. (Fig. 2.)

The couple was calibrated against ice, water, aniline, naphthalene, mercury and other liquids. The potentiometric arrangements permitted the temperatures to be read to 0·2° C. A little irregularity occurred in the earlier experiments owing to the use of soft soldered

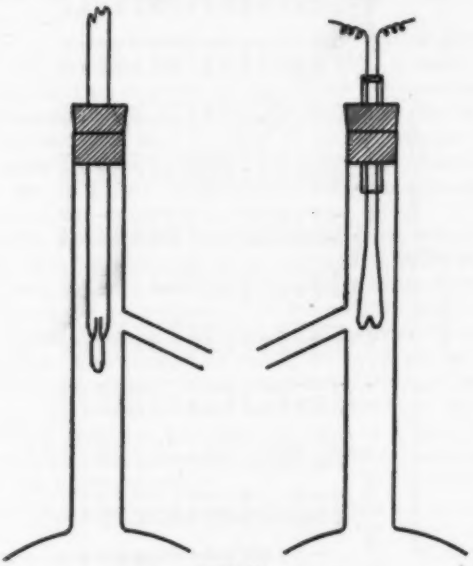


FIG. 2.

junctions, but after silver soldering was employed no further trouble was experienced.

In order to avoid the summation of the thermometer error and exposed stem correction the thermometer was calibrated against the thermo couple in an oil bath, the thermometer being under as nearly as possible the same exposed stem conditions as in an actual Engler distillation. In Table 4 are given the results of distilling various purely pure liquids, first with a mercurial thermometer and next with a thermo couple. In each case the first column gives the corrected thermometer readings, the second column the thermo couple reading, and the third gives the "lag."

TABLE 4.

Thermometer Lags in distillation of "pure" liquids.

% Distilled.	Water.		Methyl Alcohol.		Acetone.		Heptane.		Benzene.		Toluene.	
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Drop A	99·4	100·0	64·3	0·8	55·4	0·8	96·4	1·8	76·1	4·1	107·8	2·3
B	99·7	100·0	64·6	0·7	55·6	0·6	97·4	0·9	80·2	1·0	109·0	1·1
1%	99·8	100·0	65·3	0·5	55·7	0·5	97·6	0·7	80·4	1·0	109·4	0·9
2%	99·8	100·0	65·0	0·5	55·2	0·5	97·6	0·7	80·4	0·9	109·6	0·7
5%	99·9	100·0	65·0	0·2	55·8	0·4	97·6	0·7	79·6	1·0	109·4	0·9
10%	99·9	100·0	65·3	0·2	55·9	0·4	97·6	0·7	79·7	0·9	109·6	0·7
20%	99·9	100·0	65·5	0·1	56·0	0·3	97·6	0·7	79·9	0·7	109·8	0·5
30%			65·4	0·1	56·0	0·2	97·6	0·7	80·0	0·6	110·0	0·4
40%			65·5	0·1	56·1	0·2	97·6	0·7	80·0	0·6	110·0	0·4
50%			65·4	0·2	56·1	0·1	97·7	0·6	80·1	0·5	110·0	0·4
60%			65·5	0·1	56·2	0·1	97·9	0·4	80·2	0·4	110·0	0·4
70%			65·7	0·1	56·2	nil	98·0	0·3	80·3	0·3	110·0	0·4
80%			65·6	0·1	56·2	nil	98·0	0·3	80·3	0·3		
90%			65·7	0·1	56·2	nil	98·0	0·3	80·3	0·3		
95%			65·8	0·1	56·3	−0·1	98·0	0·3	80·4	0·2		
Dry			65·9	0·1	56·2	0·1	98·0	0·3	80·4	0·2		
			66·1	0·1	56·3	0·1	98·1	0·2	80·4	0·2		
			66·2	0·1	56·4	0·1	98·1	0·2	80·4	0·2		
			66·4	0·2	56·4	nil	98·1	0·2	80·4	0·2		
			66·6	0·2	56·4	nil	98·3	0·2	80·4	0·2		
			67·4	nil	56·4	0·1	98·1	0·2	80·5	0·2		
			68·9	−0·5	56·5	0·1	98·3	0·2	80·5	0·1		
			69·4	0·5	56·6	0·1	98·3	nil	80·5	0·3		
			78·7	78·3	−0·4	58·4	59·4	1·0	98·3	98·4	0·1	80·9	81·1	0·2

Drop A refers to the first drop from the side tube of the distilling flask, and B that from the end of the condenser. The thermometer readings are corrected by the curve obtained against the thermo-couple in an oil bath. No barometer corrections have been made, since these are purely additive and do not affect the lag figures.

The extremely small lag of the thermo-couple is shown by the fact that for a well-purified liquid such as the heptane employed, the distillation curve is absolutely straight from drop A onwards. It was observed that this steady temperature was attained several seconds before the first drop—in fact, within a second of the vapour reaching the junction.

The table also shows that the apparent lack of homogeneity of a purified liquid, as shown by a distillation with a mercury thermometer, may have no existence in fact. This has some bearing on such specifications of commercially pure liquids as call for 90 per cent. or 95 per cent. to distil with 0·5° C. or some similar range.

Various experiments were tried with heptane in order to determine how the indicated temperatures were affected by small modifications of the apparatus.

For example, a very light paper cone was tried just above the thermometer bulb with the idea of preventing the liquid condensed on the stem from draining back on to the bulb. It was thought that this would lessen the lag observed, but the contrary was the case.

The thermometer temperature was found to rise 0·2° C. if the neck of the flask were wrapped in cotton wool. A similar rise was not found with the couple. Wrapping the junction of the couple with cotton wool produced no effect. If, however, the couple instead of being bare was inserted in a piece of 5 mm. diameter glass tube closed at the lower end notable differences were found, as shown in the following list:—

Thermo-couple tests with heptane.

	° C.
Couple bare. c. wool round neck of flask	98·8
„ bare no wool round neck of flask	98·8
„ with dry wool round junction	98·8
„ with wetted wood round junction	98·8
„ near side of neck of flask	98·8
„ with junction pointing down	98·8
„ in empty sealed glass tube	95·8
„ in mercury in glass tube	98·4
„ in wax in glass tube	97·8

Distillation of Mixed Liquids.

Thermometer D was used. The lags as before are the difference between the thermo-couple and thermometer readings obtained in successive experiments, and are therefore burdened with a double experimental error.

TABLE 5.

Pratt's No. 1 Petrol.

% Distilled.	Thermometer.	Couple.	Lag.
Drop A	42·4	53·0	10·6
B	50·0	59·0	9·0
1	60·4	65·6	5·2
2	65·5	68·8	3·3
5	72·3	74·0	1·7
10	78·4	79·3	0·9
20	86·4	87·7	1·3
30	93·7	94·7	1·0
40	100·7	100·7	—
50	106·8	107·1	0·3
60	113·4	113·9	0·5
70	121·0	121·3	0·3
80	130·7	131·6	0·9
90	146·4	147·0	0·6
95	161·3	164·3	3·0
Dry	183·3	184·8	1·5

TABLE 6.

Shell Petrol.

% distilled.	Thermometer.	Couple.	Lag.
Drop A	45·4	54·6	9·2
B	54·4	62·7	8·3
1	68·5	70·9	2·4
2	72·0	72·8	0·8
5	79·1	80·0	0·9
10	85·3	86·7	1·4
20	94·9	95·1	0·2
30	102·4	101·9	—0·5
40	108·9	109·1	0·2
50	115·2	115·6	0·4
60	122·0	123·8	—1·8
70	130·5	132·6	1·1
80	140·6	140·6	—
90	153·6	154·7	1·1
95	166·7	169·4	2·7
Dry	185·4	190·5	5·1

TABLE 7.

Discol Fuel.

% distilled.	Thermometer.	Couple.	Lag.
Drop A	68·0	70·2	2·2
B	69·7	71·1	1·4
1	70·3	71·3	1·0
2	70·4	71·5	1·1
5	70·7	71·8	1·1
10	71·3	72·4	1·1
20	72·2	72·9	0·7
30	73·1	73·9	0·8
40	73·8	74·5	0·7
50	74·7	75·6	0·9
60	75·7	76·6	0·9
70	77·4	78·6	1·2
75	78·6	81·2	2·6

% distilled.	Thermometer.	Couple.	Lag.
Drop 76	79·1	83·2	4·1
77	80·1	82·4	2·3
78	81·6	137·5	55·9
79	124·0	143·3	19·3
80	134·2	146·0	11·8
81	140·3	149·5	9·2
82	143·9	153·7	9·8
85	155·6	161·1	5·5
90	160·0	172·5	3·5
95	180·7	184·9	4·2
Dry	196·8	200·5	3·7

TABLE 8.

Kerosene.

% distilled.	Thermometer.	Couple.	Lag.
Drop A	154·6	170·1	15·5
B	165·9	177·1	11·2
1	173·0	180·7	7·7
2	176·1	183·2	7·1
5	180·1	184·2	4·1
10	185·1	188·8	3·7
20	192·0	195·0	3·0
30	199·7	201·3	1·6

In Table 9 B.P. petrol was used throughout. The experiments marked (*b*) are those in which the thermometer was lowered 1 in. from its normal position. The difference caused by this variation is surprisingly small.

In the experiment marked (*a*) a small tube sealed at one end was slipped over the thermometer bulb. The tube was selected to fit the bulb as nearly as possible. A little mercury was used to fill the small space between tube and bulb.

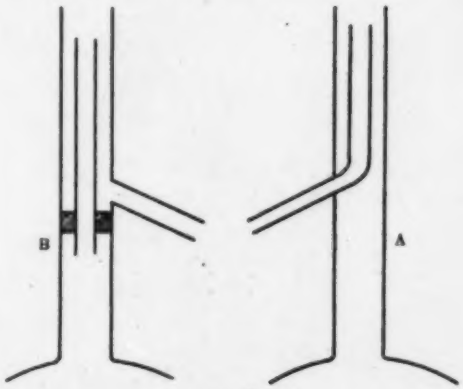


FIG. 3.

TABLE 9.

Logs of various thermometers in Engler distillation of B.P. Petrol.

% Distilled.	Couple.	D	243137.	234137 (b)	243133.	244381.	102.	23250.	23250 (b)	4.	6.	13.	243133 (a)
Drop A	57·8	14·4	13·7	13·1	15·2	15·7	17·7	18·3	13·3	16·8	20·8	19·8	23·3
B	63·5	10·1	10·3	8·1	11·9	13·9	14·3	14·0	10·6	7·7	8·0	8·8	19·4
1%	71·5	7·0	6·6	5·2	7·6	9·8	9·4	9·8	8·3	5·1	5·7	5·8	12·9
2%	73·5	6·0	5·8	4·2	6·8	7·8	7·0	8·7	6·0	4·7	4·8	4·4	10·8
5%	77·1	5·1	4·3	2·6	4·6	6·0	6·1	6·8	3·9	3·9	3·9	3·5	7·1
10%	81·1	3·5	3·3	1·7	3·4	4·3	4·5	4·7	2·5	3·3	3·4	2·9	5·2
20%	87·5	1·9	2·4	0·3	1·9	2·6	2·9	3·2	0·1	1·9	2·2	1·7	2·7
30%	95·0	2·3	2·0	0·6	2·0	3·0	3·1	3·3	0·5	2·0	2·0	2·1	2·3
40%	100·9	1·2	1·1	−0·2	0·7	1·8	2·3	1·7	−0·6	0·9	0·9	0·9	1·3
50%	107·6	0·8	0·6	−0·9	0·2	1·1	0·8	1·4	−1·7	0·9	0·6	0·9	0·4
60%	116·0	1·1	1·4	−0·3	0·6	1·9	2·1	2·1	−0·6	1·8	1·6	1·9	1·2
70%	124·8	1·8	1·0	−0·9	1·0	1·9	2·7	2·7	−1·2	1·6	1·6	1·8	1·2
80%	136·0	1·8	2·3	0·3	1·6	3·0	3·6	3·1	0·9	3·0	2·4	3·1	2·3
90%	150·6	1·6	1·3	0·5	1·5	2·7	2·9	2·6	0·7	2·9	2·6	2·9	2·4
95%	165·2	1·9	2·2	1·0	2·7	3·5	4·1	3·7	2·2	4·2	2·6	3·4	4·6
Dry	183·6	4·3	5·4	3·3	5·9	6·9	0·7	8·4	4·8	7·6	6·6	7·1	11·1

Attempts were made to devise a distilling flask which would eliminate, or at any rate reduce, the thermometric lag. Two forms tried are indicated in Fig. 3. The results in two experiments are shown in Table 10 below. Pratt's No. 1 petrol was employed.

TABLE 10.

	Couple.	Lag. a.	Lag. b.	Ordinary flask.
Drop A	53·4	24·1	—2·2	12·4
B	58·4	24·9	—1·8	8·5
1%	65·6	13·3	—4·2	2·9
2%	68·8	11·2	—3·5	2·8
5%	73·6	6·0	—3·5	1·9
10%	78·8	2·6	—4·1	1·3
20%	87·7	2·0	—2·8	1·0
30%	94·7	1·2	—1·1	0·8
40%	100·7	0·5	—0·6	0·5
50%	107·1	0·8	—1·1	1·1
60%	113·9	0·7	—0·5	1·1
70%	121·3	0·3	—0·6	1·3
80%	131·6	1·1	—0·8	1·8
90%	147·0	1·5	—2·9	2·4
95%	164·3	3·5	—7·5	5·0
Dry	184·8	10·2	4·5	7·6

It will be noticed that with form (*b*) over-correction takes place. The results did not seem sufficiently promising to justify further attempts in this direction. Experiments were also made in which the thermometer was lowered 1½ ins. from the normal position, but the lag was only reduced to about two-thirds of its usual values.

In order to calculate the lag of a thermometer in a distillation it is obviously necessary to know :—

(*a*) The speed factor K.

(*b*) The initial temperature of the thermometer at the instant before the vapour reaches the bulb.

(*c*) The temperature of the vapour at any moment from and after the instant the vapour reaches the bulb.

For the first factor we have taken the mean of the determined values of k for the solid stem thermometers in heptane. Since the latent heats of petrol spirits differ little among themselves and from heptane this mean value of k will differ little from the true value during distillation.

The initial temperature of the thermometer just before the vapour reaches its bulb was determined for the B.P. spirit with which the results given in Table 9 were obtained. By taking the time temperature curve of the thermometer in the "pre-drop" period of distillation the temperature shoots up quickly when the vapour arrives at the bulb. The thermometer indication just before the sudden rise is the initial temperature required. This need not be known very accurately as a matter of fact.

The third requirement was fulfilled by making a distillation of the B.P. petrol, using the thermo couple and timing the distillation from the moment the vapour just reached the junction. The lag of the couple is so small that there is no difficulty in getting a reading within a fraction of a second from this instant. Since a distillation of this character has probably not been recorded before the figures obtained are given below :—

TABLE 10.

Time.	°C.	Remarks.
0 secs.	54·6	
10 „	58·3	Drop A. 12 secs.
20 „	63·2	
30 „	66·4	Drop B. 28 secs.
40 „	67·6	
50 „	68·9	
60 „	70·1	
2 mins.	75·9	
3 „	78·4	
4 „	81·5	10% distilled.
5 „	83·0	
6 „	86·1	
7 „	88·1	
8 „	91·2	24% „
9 „	94·4	
10 „	97·0	
12 „	102·3	40% „
14 „	107·4	
16 „	112·2	55% „
18 „	118·9	
20 „	126·1	70% „
22 „	133·7	
24 „	142·4	85·4% „
25 „	148·0	
26 „	156·0	
27 „	170·7	
27 mins. 35 secs.	184·8	Dry 98%

Modifying our original equation to allow for the fact that T, the vapour temperature, is now not constant but a function of the time, we must write :—

$$d\theta/dt = k\{f(t) - \theta\}$$

Unfortunately, in spite of a good deal of juggling, no simple function could be found to represent the shape of the distillation curve, or even a large proportion of it at all nearly. It was therefore thought better to deal with the curve over such small time intervals that the portions of the curve intercepted could be considered as straight lines. We may then write :—

$$d\theta/dt = k(a + bt - \theta)$$

where a = temperature of vapour at start of time interval and

bt = temperature rise over the interval. Integrating gives :—

$$\theta = a + bt - b/k + (\theta_0 + b/k - a)e^{-kt}$$

θ_0 being the thermometer reading at start of time interval.

This result is worth considering in some detail : $a + bt$ is the final temperature of the vapour. Hence the lag is given by the expression :—

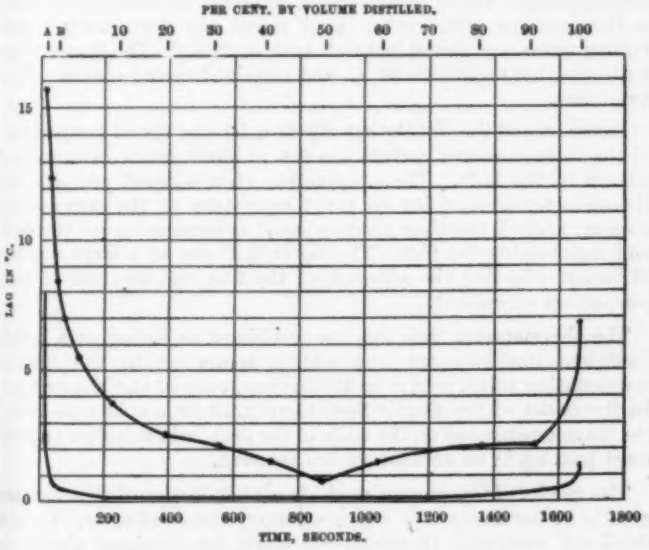
$$b/k - (\theta_0 + b/k - a)e^{-kt}$$

Taking our time interval as 10 seconds and $k = 0{\cdot}33$, this becomes

$$b/k - (\theta_0 + b/k - a)\cdot 0369$$

After about 20 seconds the latter portion of the expression becomes negligible—*i.e.*, less than 0·1°C. The lag is then practically entirely dependent on b/k, which is simply the lag arising from the rate of rise of the vapour temperature. The expression involving θ_0 is the lag arising from the initial temperature of the thermometer.

In Fig. 4 are given the curves of the mean lags observed for the six solid stem thermometers and also the lag calculated by taking



UPPER CURVE = OBSERVED LAG ON MEAN PETROL.
LOWER CURSE = CALCULATED LAG ON MEAN PETROL.

FIG. 4.

10-second intervals. It may be noted that this mode of calculation tends to give slightly high results in the initial stages of distillation and slightly low results in the later stages.

The great discrepancy between the observed and calculated results will be seen at a glance. It is obvious that the thermometric lag does not account for the observed lag. On the other hand, if similar calculations be made for the "pure" liquids the results are not greatly in error taking into consideration the uncertainty in the period elapsing between the moment of the vapour reaching the bulb and drops A and B.

It can hardly be doubted that the large "lags" observed in the distillations of petrol are due to the condensation of low boiling-point fractions on the stem and bulb of the thermometer. In any distillation the continual drip of liquid from the thermometer may be observed, and this liquid is not necessarily at the temperature of the surrounding vapour.

It is well known that when the bulb of a thermometer is kept wet with a liquid the temperature shown may be well below that of the surroundings. Young, for example, describes experiments in which a thermometer with cotton wool round the bulb wetted with boiling water was placed in an air bath at 205° C. The temperature indication fell rapidly to 66° C. and remained nearly constant for a long time.

In the case of the distillation of petrol, for any rise of temperature of the thermometer a certain amount of liquid must condense and adhere to the bulb. The evaporation of this liquid prevents the thermometer from rising to the temperature of the surrounding vapour, and all the time further liquid is condensing on the bulb and maintaining the film. The lag is thus due to a large number of factors affecting the adhesion of the film and the rate of heat conduction through it.

The thermometer thus may be considered as acting as a rather inefficient dephlegmator and adding somewhat to the natural fractionation which occurs in distillations, even of the Engler type. In the outlet of the Engler flask there must be a cold zone round the thermometer and on the walls of the neck, whilst hotter vapours must pass up in an annular stream between.

The results of the present work show that Engler distillations are greatly at the mercy of a rather arbitrary source of error. Even if duplicate mercurial thermometers could be obtained absolutely identical, the temperature recorded, particularly in the early stages of the distillation, may vary considerably with the initial rate of heating. Electrical measurement of temperature would un-

doubtedly tend to greater accuracy and uniformity. It is possible a direct reading instrument could be produced covering the usual range, say, 40°–270° C., but one would need to be very sanguine to entertain any hope that such an instrument would be widely adopted. In view, however, of the fact that a great many disputes arise in the industry from the variations which occur in this test, some such suggestion is perhaps worth consideration by those concerns interested.

The authors wish to acknowledge the financial assistance received from the Distillers Company, Limited, and the Fuel Research Board of the Department of Scientific and Industrial Research towards the expenses of this research.

The Manufacture of Carbon Black in Canada.*

By R. T. Elworthy.

Carbon black is a material of considerable importance in the printing ink and rubber industries, both in Europe and America. Its production is practically confined to the North American Continent, where large supplies of natural gas are found.

The name carbon black is reserved for the light, fluffy, black powder, formed by the incomplete combustion of natural gas, and the product so obtained has properties which are not possessed by other forms of black, such as lamp black or bone black.

Uses.—The fineness of division of the carbon black particles accounts for its great value as a filler in all kinds of rubber goods, such as tyres, boots, shoes, goloshes, soles and heels, hose sheeting, etc. Automobile tyres sometimes contain as much as 20 per cent. of carbon black, and it is claimed by many manufacturers that its use greatly increases the strength and life of a tyre.

Carbon black is one of the chief constituents of printing and lithographic inks, yielding an intense black product that cannot be produced from other forms of black. Many ink manufacturers consider carbon black absolutely essential in compounding an ink that will meet modern requirements.

This material is also a constituent of varnishes and paints, typewriter ribbons and carbon paper, shoe and stove polishes, gramophone records and almost all articles in which a black filler is used.

Source.—At the present time British requirements, which amount annually to about 10,000,000 lb., are supplied from the United States. Canadian imports from the same source are about 3,000,000 lb. The American carbon black industry is located mainly in West Virginia and Louisiana, but as many of the gas fields in these States begin to show signs of decline and conservation measures become more restrictive, the industry is seeking new fields.

Canada as a Source of Supply.—Ontario and Alberta are the only provinces in Canada possessing large resources of natural gas. Most of the Ontario fields are declining, however, and the supply is rightly restricted to domestic and industrial heating.

In Alberta, the cities of Calgary, Edmonton and Medicine Hat and many of the smaller towns are supplied with the cheap natural

* Received by the High Commissioner for Canada in London from the Dominion Department of Mines, Ottawa.

gas, and in all but a few fields in Central or Southern Alberta the gas is piped to domestic consumers or is conserved for future demand.

There are four or five natural gas fields in Alberta, however, where the prospects for the establishment of a carbon black industry might be considered. These are the Many Islands field, near Medicine Hat, the Wainwright field, one hundred miles east of Edmonton, and the Peace River and Pelican Rapid fields, in Northern Alberta.

In the Wainwright and Many Islands fields, while it is believed that extensive gas sands exist, there are few wells drilled at the present time that yield large flows of gas. Another disadvantage is that the gas so far found in both these fields is of poor quality for the manufacture of carbon black and contains little or no gasoline. Transportation facilities are good. It is doubtful if permission would be granted to make carbon black in either of these areas.

Large supplies of gas are known to exist in Northern Alberta, in the Peace River and Athabaska regions. Little reliable information has been collected on its suitability for the production of carbon black or on its gasoline and helium content. Transportation presents some difficulties, though the Peace River field is served by a good railway. The chief obstacle in the successful establishment of a carbon black plant in either of these areas would be the high freight costs.

It should be borne in mind that the present demand for carbon black is limited, and that the Canadian market could be supplied by the output of two or three plants. Great Britain and the Orient are other possible customers, but the competition with the United States for this trade would be keen.

Bituminous Sands of Northern Alberta.*

By S. C. Ells.

An extensive deposit of bituminous sand outcrops at frequent intervals along the Athabaska River and certain of its tributaries in the district centering about McMurray, in Northern Alberta. The area represented by outcrops, and presumably underlaid by bituminous sand, extends for 35 to 40 miles east and west, and 100 miles north and south, between W. long. 111° and 112° 15′ and N. lat. 56° 15′ and 58°. Upwards of 250 exposures, all within 60 miles of McMurray, and representing parts of one continuous deposit, have been examined and measured. Certain of these outcrops represent portions of a deposit that, under reasonably favourable market and transportation conditions, may eventually prove commercially valuable; but only a limited portion of the area can be considered to be of present economic value if such controlling factors as thickness and character of overburden, transportation, percentage of associated bitumen, and uniformity of material are considered. Each of these factors, as well as labour, fuel and water supply should be given careful and detailed study in considering commercial development in the McMurray district.

Associated with the bituminous sand are occasional small seepages of bitumen, locally known as tar springs. These originate in the richer beds, but are not considered to be of economic importance.

It may be stated that the McMurray deposit represents the largest known occurrence of solid asphaltic material, and that it is as yet totally undeveloped. Practically all asphaltic materials and petroleum pruducts used in Canada are now imported from foreign countries.

Three possible lines along which the bituminous sand may be commercially developed are suggested :—

(1) The crude material may be used for the surfacing of streets and highways. In 1915, in order to demonstrate the merits of the material, the writer designed and laid in Edmonton, Alberta, areas of standard sheet asphalt, bitulithic and bituminous concrete. This effort marked the first attempt to commercially utilise the bituminous sand as a paving material and the result was entirely successful. The extent to which the crude material

* Received by the High Commissioner for Canada in London from the Dominion Department of Mines, Ottawa

may be used for such purposes will be largely determined by freight charges.

(2) The bitumen, which is of a high grade, might be separated from the sand aggregate and utilised for a number of recognised purposes for which such material is well adapted.

(3) The crude bituminous sand might be retorted for the recovery of crude petroleum. Such a distillation has been made, using a retort with a charged capacity of 25 pounds crude bituminous sand, and the crude petroleum was fractionally distilled and the various distillates refined. The possibilities of such distillation on a commercial scale have not been determined, but there are strong indications that the associated hydrocarbons can be successfully recovered from the bituminous sand in this manner.

Field work in the McMurray district has included the measurement of practically all outcrops and extensive core sampling throughout a large part of the area. As a result of this work it is now possible to indicate a number of areas which, on the basis of observed outcrops, appear to be best adapted to possible commercial development. Detailed topographical maps of a large part of the area are being prepared for publication.

At the present time the problem presented by the recovery of hydrocarbons from the crude bituminous sand is being studied by a number of responsible individuals and companies.

THE BRITISH EMPIRE EXHIBITION, 1924.

By the Assistant Editor

A special visit was made to the Exhibition with the object of noting the exhibits likely to be of interest in connection with petroleum, and brief particulars of these are given below.

The Exhibition is within easy access from all parts of London, being close to Wembley Park (Metropolitan Railway), Wembley Hill (L. & N.E. Railway), and Wembley (L.M. & S. Railway) stations. In addition, the L. & N.E. Railway have a station in the grounds.

The area occupied by the Exhibition is large, the total length of roadways approximating fifteen miles, and it is obvious that to examine the various exhibits in detail it is advisable to adopt a definite route and programme. It is therefore suggested that the buildings be visited in the following order, commencing from the North Entrance (Wembley Park Station):—Palace of Industry, Palace of Engineering, India, Canada, Australia, Sarawak, Malaya, New Zealand, Palace of Arts, Burmah, Gold Coast, Bermuda, West Africa, Sierra Leone, Nigeria, Palestine, South Africa, East Africa, Malta, Ceylon, Hong-Kong, British Guiana, West Indies, H.M. Government, Newfoundland, Fiji, and then through the Amusement Park back to the North Entrance. From the other entrances a slight adjustment in the starting-point of the tour will enable the same route to be followed.

For those having a limited amount of time at their disposal, and who wish to see only those exhibits dealing with the Petroleum Industry, an alternative route is suggested, covering only those buildings where such exhibits are shown, as detailed below. It must be understood that, while every endeavour has been made to include all those exhibits likely to be of particular interest to those engaged in the Petroleum Industry, the following is not published as a complete list of the various exhibits.

Bearing to the right after leaving the North Entrance, the West Gate of the

PALACE OF INDUSTRY

is straight ahead. In this building

W. J. Fraser & Co. (Stand A56b) are exhibiting a Periodic Still for experimental work, with its various fittings.

Midland Tar Distillers, Ltd. (Stand A84), and

GAS LIGHT & COKE COMPANY (Stand A65) are each showing a full range of samples of coal tar products.

BAIRD & TATLOCK, LTD. (Stand A59) are exhibiting testing apparatus, including the Standard and Admiralty types of Redwood Viscometers.

In the BRITISH EMPIRE GAS EXHIBIT samples of the oils obtained by the carbonisation of coal are shown, and in this section the NATIONAL BENZOLE COMPANY are exhibiting a model showing a coal mine, gas works, oil refinery, and the distributing arrangements for the refined oils.

Leaving the Palace of Industry by the Gate of Harmony, the Watt Gate of the

PALACE OF ENGINEERING

is directly opposite. This building contains in itself an exhibition worthy of the detailed examination of every engineer. Turning to the right to the end of Avenue 1, and proceeding down and up each avenue in turn, the exhibits likely to be of interest, in the order in which they are passed, are :—

L. GARDNER & SONS, LTD. (Stand 187, Avenue 1–2, Bay 22); type 3T6 72-h.p. Reversible Cold-Starting Semi-Diesel Engine; type HF 30-h.p. Cold-Starting Horizontal Diesel Engine; type DCR 38-h.p. 6-Cylinder Reversible Petrol and Kerosene Marine Engine.

ROBEY & Co. (Stand 202, Avenue 1, Bay 26–27). Model of Vertical Crude Oil Engine.

STERNS, LTD. (Stand 275, S.E. Block, Bay 24). Samples of Engine Oils, etc.

SMITH'S DOCK COMPANY, LTD. (Stand 139, Avenue 2–3, Bay 20–21). Burners and furnace fronts for Smith's patent oil-burning system, and a model showing a complete marine installation. A fuel-oil strainer is shown and a sectional model of a barge for the separation of oil from oil-contaminated water. Also a working model of an all-steel drilling rig, and samples of wire ropes.

WALLSEND SLIPWAY AND ENGINEERING COMPANY, LTD. (Stand 143, Avenue 2–3, Bay 16–17). Furnace fronts fitted for oil firing and for oil or coal firing; Oil burners for steam jet system and for low air pressure system; Straining, heating, and filtering apparatus for oil fuel.

TANGYES, LTD. (Stand 100, Avenue 3–4, Bay 12-13). 47 b.h.p. cold-starting heavy oil engine, and various types of pumps.

GEORGE CRADDOCK & Co., LTD. (Stand 117, Avenue 3–4, Bay 26–27). Complete range of oil-well ropes.

PETTERS, LTD. (Stand 80, Avenue 4–5, Bay 13–14). Various types of vertical and horizontal oil engines.

DORMAN, LONG & CO., LTD. (Stand 43, Avenue 5–6, Bay 10–12). Samples of coal-tar products.

G. & J. WEIR, LTD. (Stand 44, Avenue 5–6, Bay 12–15). Oil-fuel pumps for various purposes.

BLACKSTONE & CO., LTD. (Stand 52, Avenue 5, Bay 18–20). 300-h.p. solid injection oil engine in operation.

BRITISH MANNESMANN TUBE COMPANY, LTD. (Stand 64, Avenue 5–6, Bay 26–28). Sections of various joints used for oil-well casing and for pipe-lines.

RUSTON & HORNSBY, LTD. (Stand 21, Avenue 6–7, Bay 23–24). Four-cylinder open type vertical airless injection oil engine, 420 b.h.p., in operation; three-cylinder enclosed type vertical airless injection oil engine, 165 b.h.p.; 42 b.h.p. horizontal cold-starting oil engine; 7 b.h.p. petrol-paraffin engine; pumping plant operated by 2 b.h.p. petrol-paraffin engine.

HAYWARD TYLER & CO., LTD. (Stand 46, Avenue 6, Bay 15–16). Duplex cargo oil pump, 22 ins. × 14 ins. × 18 ins.; fuel oil pressure pump, 5 ins. × 3½ins. × 6 ins.; horizontal duplex fuel oil pressure pump, 5 ins. × 3 ins. × 8 ins., fitted with Twell's patent positive valve motion, in operation.

VICKERS, LTD. (Stands 1 & 2, Avenue 7–8, Bay 5–15). In the Research Department a model is shown illustrating a complete plant for the low-temperature carbonisation of coal, lignite, shale, peat, etc., on the Vickers-fusion system. A bench of 32 retorts is shown and the plant for by-product recovery and for the treatment of the recovered oils, and also for free oil obtained from wells.

VICKERS-PETTERS, LTD., are showing types of crude oil engines elsewhere on these stands.

W. BEARDMORE & CO., LTD. (Stands 3 & 4, Avenue 7–8, Bay 15–19). 120 b.h.p. Boardmore-Tosti Diesel engine in operation; three-cylinder Beardmore-Speedwell oil engine.

W. H. ALLEN, SONS & CO., LTD. (Stand 9, Avenue 8, Bay 22–23). 320 b.h.p. 4-cylinder Diesel engine; 60 b.h.p. 2-cylinder Semi-Diesel engine.

SIR W. G. ARMSTRONG-WHITWORTH & CO., LTD. (Stands 11 & 12, Avenue 7–8, Bay 24–28). Samples of coal-tar products and bituminous limestone. An interesting exhibit here is the locomotive built for the Buenos Ayres Great Southern Railway, as this is an oil-fired engine. The heating surface is 1887 sq. ft., superheater surface (inside) 410 sq. ft., the boiler pressure being 200 lb. The three cylinders are operated by Walschaert valve gear, and at 85 per cent. boiler pressure the tractive effort is 34,400 lb. The total weight of engine and tender is 134½ tons.

BABCOCK & WILLCOX, LTD. (Avenue 11-12, Bay 23-24). Furnace front and fittings for oil-fired boiler.

CROSSLEY BROS., LTD. (Avenue 13, Bay 9-10). 72-b.h.p. cold-starting crude oil engine; 14-b.h.p. two-stroke crude oil engine.

MOTORS AND CYCLES SECTION.

The following firms are showing samples of their particular brands of motor oils, the number of each exhibit being in brackets :— W. BLACKWELL OIL COMPANY (15); A. DUCKHAM & CO. (228); GAS LIGHTING IMPROVEMENT COMPANY, LTD. (25); NATIONAL BENZOLE COMPANY, LTD. (106); PRICE'S PATENT CANDLE COMPANY, LTD. (189); L. STERNS, LTD. (203); and HENRY WELLS OIL COMPANY (105).

Leaving the Palace of Engineering and turning into The Eastings, the first building on the right is occupied by SHELL-MEX, LTD. When visited this building was incomplete, but will eventually contain exhibits dealing with the "Shell" oilfields within the Empire.

The next building on the right is that of

THE ANGLO-PERSIAN OIL COMPANY

and its allied companies. The centre of the building is occupied by a model of an all-steel rotary drilling rig, and surrounding this are a number of interesting exhibits, as follows :—

Samples of Persian crude and products; relief model of fields, pipe-lines, and refinery in Southern Persia; relief model of Scottish shale-oil works, 1924, on a scale of 40 ft. to 1 in.; sectional model of Henderson oil still; sectional model of Young & Beilby retort, 1884; samples of Scottish oil-shale and products obtained therefrom; model of tank steamer, "British Merchant."

Opposite this building is the

INDIAN PAVILION,

and in the Geological Survey Section will be found a case containing samples of crude and products obtained by the Attock Oil Company.

CANADA.

In the mineral exhibit samples of Canadian crude oils are shown and also specimens of albertite and bituminous shale from Albert County and Westmoreland Counties respectively, New Brunswick.

SARAWAK.

The Sarawak Oilfields, Ltd., are exhibiting samples of Sarawak crude oil and refined products, and several models illustrating the petroleum industry of that country :—

Relief model of Lutong Refinery; model showing tanker being loaded by means of a submarine pipe-line at Lutong; model showing Well No. 1 at Miri being "brought in"; working model of all-steel standard drilling rig.

NEW ZEALAND.

The minerals of New Zealand include samples of oil-shale from Orepuki.

BURMAH PAVILION.

The Burmah Oil Company are exhibiting samples of the crude oil of Burmah, refined oils and candles.

At the back of the Burmah Pavilion, Messrs. MINERAL OILS EXTRACTION, LTD., of Finsbury Court, London, E.C., are demonstrating the destructive distillation of oil-shale and lignite by means of a Crozier retort. A unit having a throughput capacity of 20 tons per diem has been erected, and will be in operation. The retort is continuous in operation and is so arranged that the first fractionation of the oil is carried out direct from the retort, resulting in the production of semi-refined products in one operation only. Exhibition conditions will not, of course, permit the retort being operated continuously or at full capacity. Demonstrations will be given chiefly on oil-shale and lignite from Burmah, but arrangements can be made by approved firms for the treatment of shale, etc., from other sources, as may be desired.

TRINIDAD.

An interesting exhibit here is a working model of the Pitch Lake showing also the oil-field and tank farm in its vicinity.

H.M. GOVERNMENT PAVILION.

On the ground floor the Department of Scientific and Industrial Research deal chiefly with the low-temperature carbonisation of

coal, and show diagrams of experimental retorts used for this work. Coal tar films are also on view.

On the first floor, in the Department of the Government Chemist, is the apparatus used to determine the quantity of helium contained in natural gas.

On leaving the Government Building, and proceeding towards the Amusement Park, two drilling rigs will be seen.

The OIL WELL ENGINEERING COMPANY'S exhibit consists of an all-steel combination rig, which will be in operation. For rotary drilling a twin-cylinder engine is used, and for cable work a standard cable tool engine, both of which are supplied with steam from a 45-h.p. Oil Country boiler. A Stockport internal-combustion drilling engine, and the usual complement of drilling tools, casing, slush pumps, etc., are also shown.

Messrs. VICKERS, LTD., are exhibiting a two-speed, chain-drive rotary drilling rig, with a 6-in. drum shaft and a 5-in. line shaft, capable of drilling to a depth of over one mile. The derrick is of steel, 106 ft. in height, and constructed for a working load of 100 tons. Power is supplied either from a 50-h.p. twin-cylinder steam engine or a 120-h.p. electric motor, the steam for the engine being furnished from an oil-fired boiler. Two types of mud-pumps are installed, one operated by steam and the other an electrically driven Vickers-Pavic pump. This rig will be in operation, the initial diameter of the well being 24 ins. .

An item of particular interest in connection with this exhibit is the tools which were used in the drilling of Colonel Drake's historic well, and for comparison these are shown alongside a string of modern cable tools.

DISCUSSION ON :—

Galician-Canadian Pole Tool Fishing Method.*

Mr. Cyril W. Davson writes :—

The paragraph entitled "Recovery of small objects," such as underreamer dogs, etc., does not, however, seem to solve this difficult problem.

The suction sand-pump, of which there are several makes on the market, will undoubtedly withdraw small pieces of iron, but the real problem is to withdraw one or possibly two underreamer dogs from a hole.

The basket casing for such a purpose as this is a crude tool.

The Devil's Pitch Fork may be considered to be as near as possible a perfect tool for the above purpose when the hole is dry. This tool consists of 12 prongs attached to springs, 8 arranged in a circle and 4 in the middle of the circle, the springs and the top portion of the prongs being enclosed in a case.

After running an impression block, if the underreamer dog or other lost object is not in a position to allow it to be pulled through the casing, it must be spudded into such a position. The Devil's Pitch Fork is then lowered until the prongs slide gently over the object and no matter what shape the object may be, if it can be pulled through the casing, it will be immediately removed.

The Roger Grab, on the other hand, is a much more substantial tool. It consists of a rod working on a toggle. The toggle is attached to legs which have teeth at their extremities. Above the yoke to which the legs are attached is a powerful spring, which closes the legs by means of the toggle and thus holds the object. In lowering down the grab into the hole the legs are kept apart by pieces of wood. On striking the object in the hole the wood is knocked out and the object is held between the teeth of the legs by the action of the spring.

The Devil's Pitch Fork should not (generally speaking) be used in cavings as it is too slender to stand the jarring, but the Roger Grab can be used in any condition of hole as it is solid enough to stand the jarring.

The Helrazer is an electric fishing tool operating an electro-magnet. The batteries are entirely enclosed and the Helrazer can be used either in wet or dry holes and for any small or large pieces of metal. Special attachments are available for picking up

* Journal 40, p. 397. December, 1923.

underreamer cutters, also special slip catches, and magnetic prongs for picking up iron and steel casing and tubing and bailers. For example, a bit lost in the hole and lying over against the side in such a position that no tool can get over it to pick it up would, on lowering a Helrazer, be immediately pulled towards the centre of the hole and then pulled right out of the well. This has actually been done by Helrazers, a matter of an hour or two saving possibly weeks of difficult fishing.

It is a well known fact in fishing that it is rarely the original fishing job that is the most difficult, but those that follow afterwards and complicate the problem either by the unskilful or even the skilful use of the wrong tools. The following sizes will be found suitable to keep in stock when either inserted joint or collared casing is in use :—

Devil's Pitch Fork :	One each sizes 8 in., 10 in. and 15 in.
Roger Grab :	One each for sizes 8¼ in., 10 in. and 13 in. (O.D.).
Helrazer :	One each for 5⅛ in., 8¼ in. and 12½ in.

As when small sizes of casing are used it is quite possible that a Helrazer may prove to be not only the only tool that will solve the problem rapidly, but the only tool that will solve it at all.

Helrazers should be complete with various attachments and a good supply of spare batteries.

I note that the paper is confined to fishing methods with Galician-Canadian pole tool plants, and therefore comparison between this and other drilling plants would be irrelevant, but I am in agreement with the member who suggests that the pole tool system should "give way to some more modern system, particularly at great depths."

I am also in agreement with the member who points out the vital importance of cleanliness at rigs, from the lack of which so much confusion in actual drilling operations and also from the point of view of store keeping arises.

Mr. Albert Millar, in reply, wrote :—

I quite agree with Mr. C. W. Davson that the Devil's Pitch Fork is a good instrument for recovering small objects from dry and moderately shallow holes of large diameter, but this instrument is certainly not to be recommended for fishing in deep holes of 4000 to 5000 ft. having diameters of 5 to 7 in., the drawback being delicacy of construction and the difficulty of regulating the amount of pressure which is being put upon this tool at greater depths. The same remarks apply to the Roger Grab.

It must be borne in mind that it is possible to use almost any tool in large diameter holes of from 1000 to 1500 ft. deep, but the use

of complicated fishing tools made up of many parts, and especially where their action is dependent upon springs, generally results in further complications in deep holes.

The Helrazer or electro magnet should certainly prove a useful fishing instrument, but I believe there is still a great deal of room for improvement in its construction, and before these improvements are carried out it will not be a popular tool with practical oilfield men.

The watchword in oilwell tool construction should be simplicity and robustness; this is often not the case, and some operators seem inclined to select tools of a showy and complicated design.

When small objects are lost, such as underreamer cutters (dogs), sand pump valves, etc., one should consider whether it is advisable to fish for these or to drill them to one side. From personal experience I have found it is generally time lost to commence fishing, and by far the simpler and quicker method is to sidetrack the lost objects. For instance, in a deep well over 4000 ft. seven underreamer cutters were left behind, and were drilled past in under 24 hours.

REVIEW.

NEW AND REVISED TAG MANUAL FOR INSPECTORS OF PETROLEUM. By R. M. Wilhelm. 18th Edition. New York: Tagliabue Co.

Tagliabue's manual is known and used by almost every oil company in the United States, and additional tables likely to be useful to the oil chemist and inspector are included in this revise. The tests are either standards adopted by the A.S.T.M. or the U.S. Inter-Departmental Petroleum Specification Committee. Particular attention is drawn to the A.P.I. revised gravity temperature corrections computed by the U.S. Bureau of Standards. The contents include gravity, colour, viscosity of various products, distillation tests, acidity in gasoline, flash and fire points, carbon residue, water, B.S., corrosion, sulphur and doctor tests for gasoline, unsaturateds, boiling points, flow tests, vapour tensions, etc., together with a mass of useful tabulated matter. In view of the publication of the Institution's Standard Tests this volume will be of considerable interest. A. E. D.

We have received from the U.S. Department of Commerce preprints of the ollowing specifications :—

No. 83 for Pitch for water-proofing and damp-proofing. Very full details are given relative to sampling, melting point, ductility, specific gravity, free carbon, distillation test and properties of distillates.

No. 84 deals with the nature of Asphalt for mineral surfaced roofing and gives a full description of the technique of the Dow ductility determination.

No. 87 relates to Asphalt Primer for roofing and water-proofing, and describes the determination and examination of the asphaltic base, detailing procedure for melting point, penetration and examination of solvent matter.

A. E. D.